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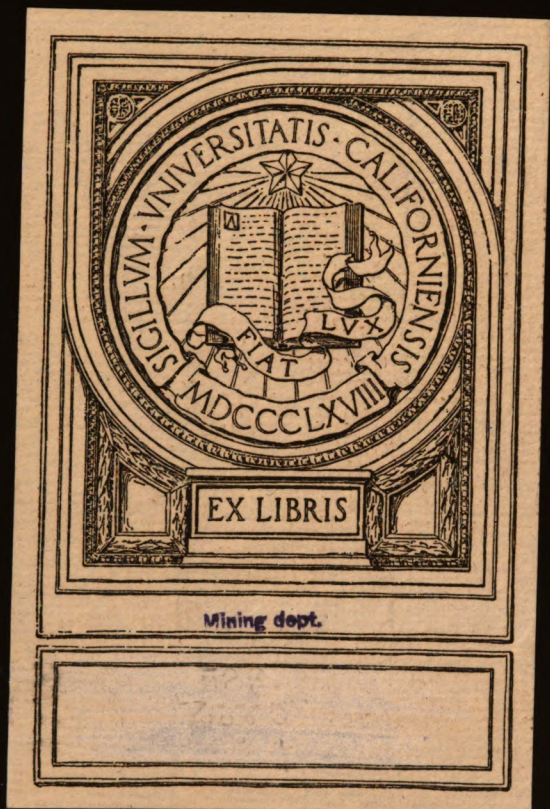
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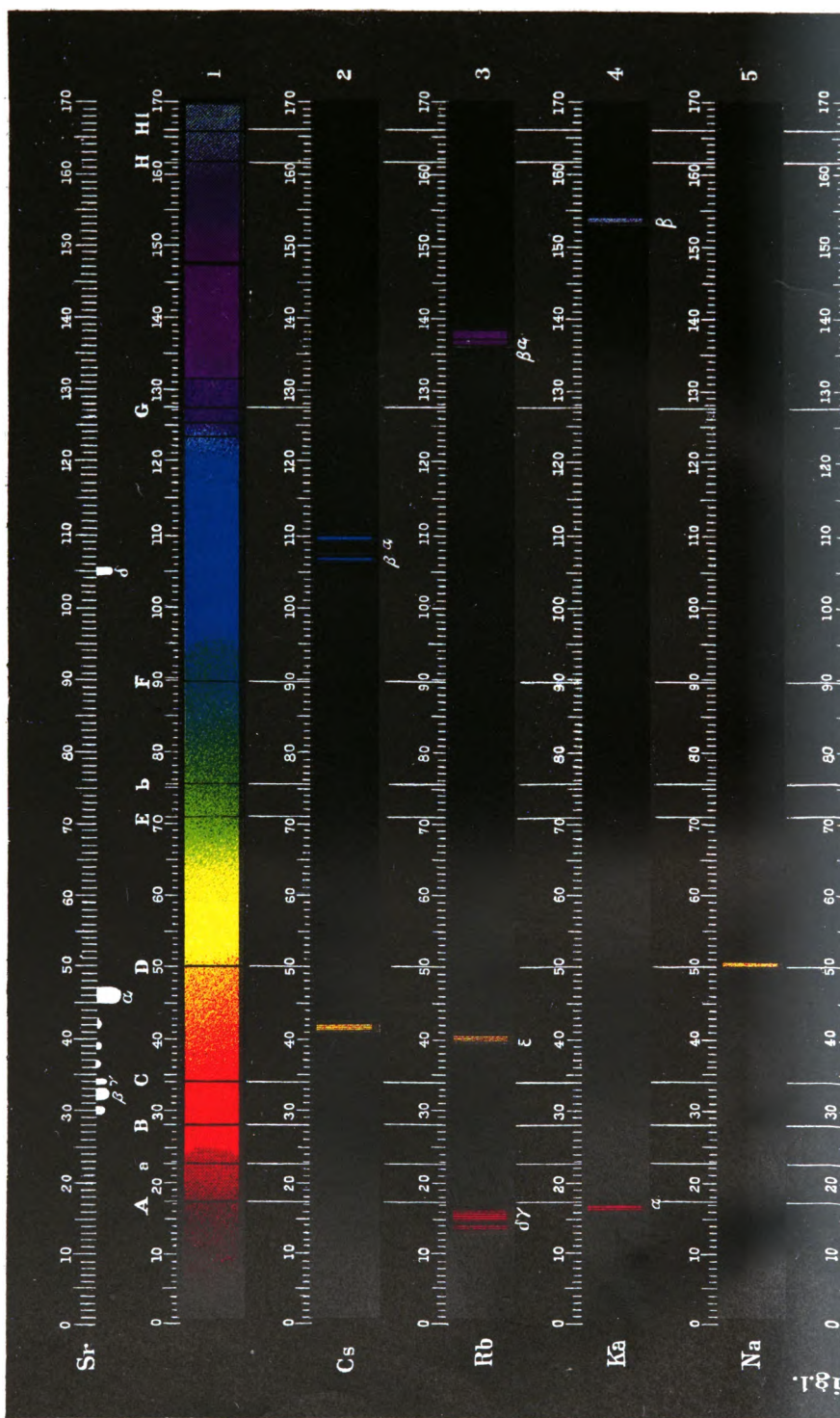


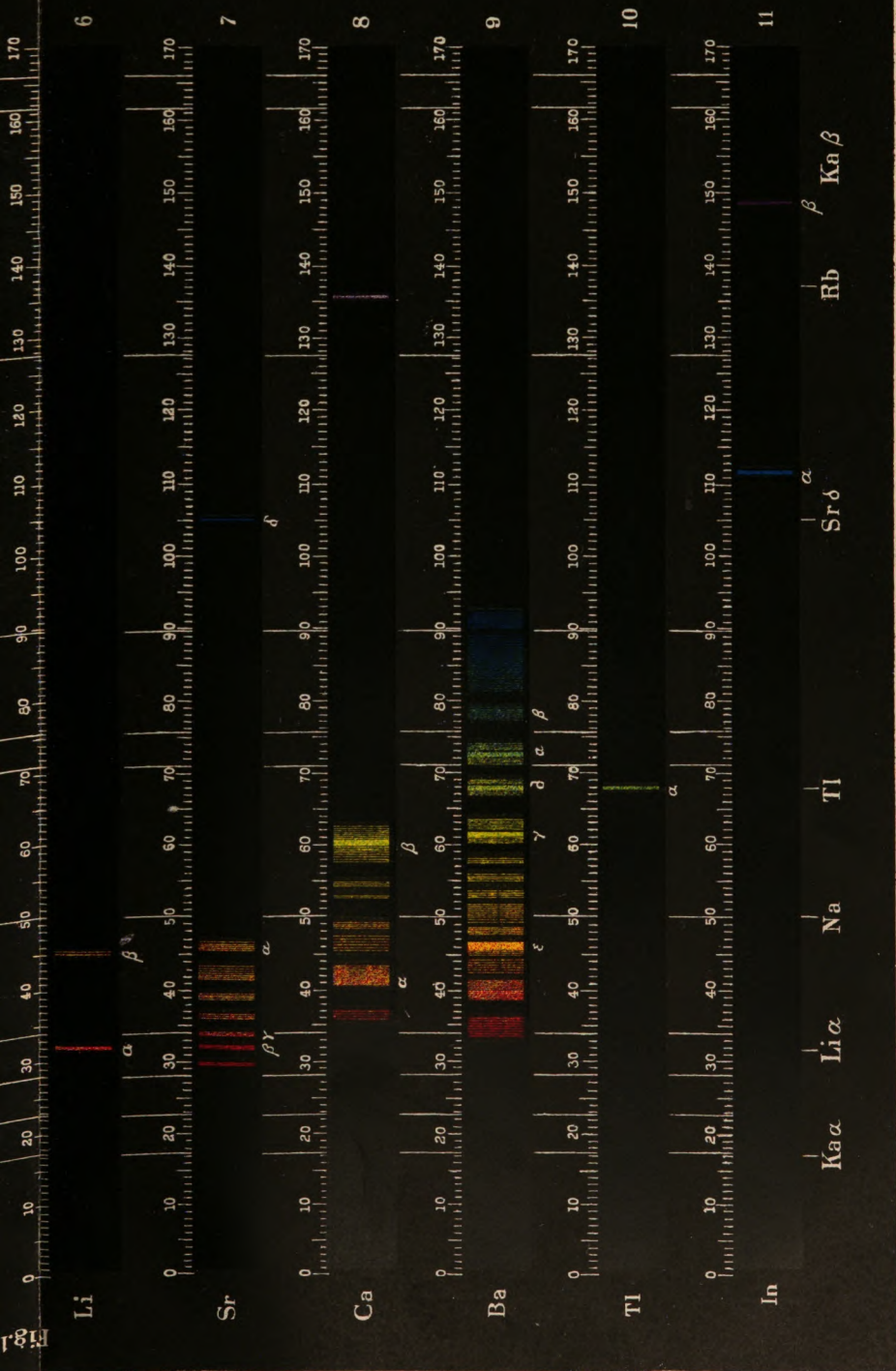












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INTRODUCTION  
TO THE  
RARER ELEMENTS.

BY  
PHILIP E. BROWNING, PH.D.,  
*Assistant Professor of Chemistry, Kent Chemical Laboratory,  
Yale University.*

*THIRD EDITION, THOROUGHLY REVISED.*

FIRST THOUSAND

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NEW YORK  
JOHN WILEY & SONS, INC.  
LONDON: CHAPMAN & HALL, LIMITED  
1914

QD171  
B8  
1912

MINING DEPT.

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## PREFACE TO THE THIRD EDITION.

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IN attempting again to bring this work up to date for a new edition, the author has made numerous changes and additions throughout the book. The chapter on qualitative separation has been considerably enlarged by the inclusion of new analytical diagrams, together with some working directions and notes. The chapter on technical applications, also, has been much expanded by the addition of new material. A table of spectroscopic lines, and plates showing typical spectra have been added.

For helpful suggestions in selecting the spectroscopic material the author acknowledges his indebtedness to Professor H. S. Uhler of Yale University. His thanks are again due, also, to many of those whose kindness has been mentioned in prefaces to previous editions.

NEW HAVEN, CONN., October, 1912.

iii





## PREFACE TO THE SECOND EDITION.

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DURING the five years that have elapsed since the appearance of the first edition of this book, the chemistry of the rarer elements has undergone no small measure of development. In that division of the field known as the rare earths, Dr. C. Richard Böhm's *Darstellung der seltenen Erden*, in two volumes of about five hundred pages each, has given to chemists some conception of the mass of work which, up to that time, had been done; and since the publication of those volumes the activity along this line has not abated. During the same period the study of the radio elements has developed a well-defined department of research, and the rare metals vanadium, tungsten and tantalum have become important members of the chemical family on account of their technical applications. These examples illustrate the recent advances which demand recognition even in a handbook of small compass.

In presenting this edition the author makes grateful acknowledgment to Dr. B. B. Boltwood of Yale University for his contribution of the chapter on Radio Elements, to Dr. C. L. Parsons of New Hampshire College for kindly suggestions regarding the revision of the chapter on Beryllium, to members of the author's recent classes in the rarer elements for their experimental work leading to the selection of separation methods, to the critics of the first edition for useful hints, and to his wife for much painstaking work upon the preparation of the manuscript for publication.

NEW HAVEN, CONN, October, 1908.

v



## PREFACE TO FIRST EDITION.

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THIS small volume, prepared from material used by the author in a short lecture course given at Yale University, is intended to serve as a convenient handbook in the introductory study of the rarer elements; that is, of those elements which are not always taken up in a general course in chemistry. No attempt has been made to treat any part of the subject exhaustively, but enough references have been given to furnish a point of departure for the student who wishes to investigate for himself. Experimental work has been included except in the case of those elements which are unavailable, either because of their scarcity or because of the difficulty of isolating them.

The author has drawn freely upon chemical journals and standard general works. In his treatment of the rare earths he has made especial use of Herzfeld and Korn's *Chemie der seltenen Erden* and Truchot's *Les Terres Rares*, works which he gladly recommends. He gratefully acknowledges the valuable assistance of his wife in preparing this material for the press.

NEW HAVEN CONN., April, 1903.

vii



## TABLE OF CONTENTS.

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CHAPTER	PAGE
I. THE ALKALIES .....	I
II. BERYLLIUM .....	17
III. THE RADIO-ELEMENTS. ....	25
IV. THE RARE EARTHS .....	35
V. GALLIUM, INDIUM, THALLIUM .....	82
VI. TITANIUM, GERMANIUM .....	96
VII. VANADIUM, NIOBIUM, TANTALUM .....	107
VIII. MOLYBDENUM, TUNGSTEN, URANIUM .....	125
IX. SELENIUM, TELLURIUM .....	144
X. THE PLATINUM METALS, GOLD .....	161
XI. THE RARE GASES OF THE ATMOSPHERE .....	190
XII. TECHNICAL APPLICATIONS .....	196
XIII. QUALITATIVE SEPARATION .....	205
XIV. SPECTROSCOPIC TABLES .....	223
INDEX .....	231





## INDEXES TO THE LITERATURE OF CERTAIN ELEMENTS.

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- Beryllium, The Chemistry and Literature of (1798-1908); Parsons-  
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- Cerium, Index to the Literature of (1751-184); Magee. Smithsonian  
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- Gallium, Index to the Literature of (1876-1903); Browning. Smith-  
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- Vanadins, Die Literatur des (1804-1905); Prandtl. Hamburg, Leopold Voss, 1906.
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- Die Chemie des Thoriums; Koppel. Sammlung chemischer Vorträge, Band VI. Pub. by Ferd. Enke, Stuttgart, 1901.
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- La Chimie de L'Uranium (1872-1902); Oechsner de Coninck. Pub. by Masson et Cie., Paris, 1902.
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- Le Vanadium; P. Nicolardot. Pub. by Masson et Cie., Paris.
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## THE RARER ELEMENTS

### CHAPTER I.

#### THE ALKALIES.

##### LITHIUM, Li, 6.94.

**Discovery.** In 1817 Arfvedson, working in Berzelius's laboratory upon a petalite from Uto, Sweden, discovered an alkali which he found to differ from those already known in the following particulars: (1) in the low fusing points of the chloride and sulphate; (2) in the hygroscopic character of the chloride; and (3) in the insolubility of the carbonate. In his analysis of the mineral it had remained associated with sodium, not being precipitated by tartaric acid. To the newly discovered element the name Lithium was given, from *lithos, stone*, because it differed from sodium and potassium in having a mineral rather than a vegetable origin (Ann. der Phys. u. Chem. (1818), xxix, 229; Ann. Chim. Phys. [2] x, 82). It has since been found, however, not only in the mineral kingdom, but in the vegetable and animal kingdoms also.

**Occurrence.** Lithium is found combined as follows:

(1) In minerals:

Petalite,	$\text{LiAl}(\text{Si}_2\text{O}_5)_2$ ,	contains 2-5%* $\text{Li}_2\text{O}$ .
<i>Spodumene</i> ,†	$\text{LiAl}(\text{SiO}_3)_2$ ,	" 4-8% "
<i>Lepidolite</i> ,	$\text{R}_3\text{Al}(\text{SiO}_3)_3$ ,	" 4-6% "
Zinnwaldite, (K,Li) <sub>3</sub> FeAl <sub>3</sub> Si <sub>5</sub> O <sub>16</sub> (OH,F) <sub>2</sub> ,	"	3-4% "
Cryolithionite, $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$ ,	"	5-6% Li
Cryophyllite, complex silicate, <i>vid.</i> Zinnwaldite,	contains 4-5% $\text{Li}_2\text{O}$ .	

\* In the tabulation of percentages the nearest whole numbers have generally been used in this book.

† The more important mineral sources are indicated by italics.



Irvingite, complex silicate, contains 4-5%  $\text{Li}_2\text{O}$ .

Polyolithionite, complex silicates, *vid.* Zinnwaldite, contains about 9%  $\text{Li}_2\text{O}$ .

Beryl,  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ , contains 0-1%  $\text{Li}_2\text{O}$ .

*Triphylite*,  $\text{Li}(\text{Fe}, \text{Mn})\text{PO}_4$ , " 8-9% "

*Lithiophilite*,  $\text{Li}(\text{Mn}, \text{Fe})\text{PO}_4$ , " 8-9% "

*Amblygonite*,  $\text{Li}(\text{AlF})\text{PO}_4$ , " 8-10% "

*Natramblygonite*,  $\text{NaAl}(\text{OH})\text{PO}_4$ , " 3-4% "

Small amounts of lithium are found also in some varieties of tourmaline, in epidote, muscovite, orthoclase, and psilomelane.

(2) In certain mineral waters, among which are Dürkheim, Kissingen, Baden-Baden, Bilin, Assmannshausen, Tarasp, Kreuznach, Salzschrif, Aachen, Selters, Wildbad, Ems, Homburg, Karlsbad, Marienbad, Egger-Franzenbad, Wheal Clifford, Bad Orb, Sciacca, Salsomaggiore.

(3) In seaweed, tobacco, cacao, coffee, and sugarcane; in milk, human blood, and muscular tissue; in meteorites.

**Extraction.** Lithium may be extracted from minerals by the following methods:

(1) *From triphylite or lithiophilite.* The coarsely ground mineral is dissolved in hydrochloric acid to which nitric acid is gradually added, and the solution obtained is treated with a sufficient amount of ferric chloride to unite with all the phosphoric acid present. This solution is evaporated to dryness and the residue is extracted with hot water. The extract thus obtained is treated with barium sulphide, to remove the manganese and the last traces of iron. The barium is removed by sulphuric acid, and the filtrate is evaporated with oxalic acid and ignited. The alkalis remain as carbonates (Müller).

Lithium may be separated from the other alkalis by treating the mixed carbonates with water, lithium carbonate being comparatively insoluble.

(2) *From lepidolite (or any other silicate).* The mineral is

melted at red heat in a crucible, the melted mass is cooled rapidly in water and pulverized. Sufficient water is added to give the material the consistency of paste. Hydrochloric acid of specific gravity 1.2, equal in weight to the weight of the mineral taken, is gradually added, with stirring. The mass is allowed to stand for twenty-four hours. It is then heated again to about  $100^{\circ}\text{C}$ ., with stirring, and a second portion of acid equal to the first is added. Upon several hours' heating the silica separates in the form of powder, and after treatment with nitric acid to oxidize the iron, the soluble material is separated by filtration from the silica. The filtrate is heated to the boiling-point and treated with sodium carbonate, which precipitates iron, aluminum, calcium, magnesium, manganese, etc. These are removed by filtration, and the liquid is evaporated to a small volume and filtered again if necessary. Lithium carbonate is precipitated by more sodium carbonate (Schrötter).

**The Element.** *A. Preparation.* Elementary lithium may be obtained (1) by subjecting the fused chloride or bromide to electrolysis; (2) by heating a mixture of elementary calcium and lithium chloride in the presence of hydrogen (Hackspill).

*B. Properties.* Lithium is a metallic element which has a silvery-white luster and which oxidizes in the air, though more slowly than potassium and sodium. It decomposes water at ordinary temperatures, and is light enough to float in petroleum. Its melting-point is  $180^{\circ}\text{C}$ .; its specific gravity is 0.59.

**Compounds.** *A. Typical forms.* The following are typical compounds of lithium:

Oxides,  $\text{Li}_2\text{O}$ ;  $\text{Li}_2\text{O}_2$ . 85.45.

Hydroxide,  $\text{LiOH}$ .

Carbonate,  $\text{Li}_2\text{CO}_3$ .

Chloride,  $\text{LiCl}$ .

Chlorate,  $\text{LiClO}_3 + 0.5\text{H}_2\text{O}$ .

Perchlorate,  $\text{LiClO}_4 + 3\text{H}_2\text{O}$ .

Bromide,  $\text{LiBr}$ .

Bromate,  $\text{LiBrO}_3$ .

Iodide,  $\text{LiI} + 3\text{H}_2\text{O}$ .

Iodate,  $\text{LiIO}_3 + 0.5\text{H}_2\text{O}$ .

Periodate,  $\text{LiIO}_4$ .

Fluorides,  $\text{LiF}$ ;  $\text{LiF} \cdot \text{HF}$ .

Nitride,  $\text{LiN}_3$ .

Nitrite,  $\text{LiNO}_2 + 0.5\text{H}_2\text{O}$ .

Nitrate,  $\text{LiNO}_3$ .

Sulphide,  $\text{Li}_2\text{S}$ .

Sulphite,  $\text{Li}_2\text{SO}_3$ .

Sulphates,  $\text{Li}_2\text{SO}_4$ ;  $\text{KLiSO}_4$ ;  $\text{NaLiSO}_4$ ; etc.

Phosphates,  $\text{LiH}_2\text{PO}_4$ ;  $\text{Li}_3\text{PO}_4 + 0.5\text{H}_2\text{O}$ ;  $\text{Li}_4\text{P}_2\text{O}_7$ .

Carbide,  $\text{Li}_2\text{C}_2$ .

Silicofluoride,  $\text{Li}_2\text{SiF}_6 + 2\text{H}_2\text{O}$ .

*B. Characteristics.* Most of the salts of lithium are easily soluble in water; the principal exceptions are the carbonate, the phosphate, and the fluoride, which are difficultly soluble. Lithium resembles sodium more closely than it resembles the other alkalies, in that it does not form an insoluble chloroplatinate, nor a series of alums. The nitrate and the chloride are soluble in alcohol. The compounds of lithium color the flame brilliant crimson.

*Estimation.* Lithium is usually weighed as the sulphate or chloride.

*Separation.* Lithium may be separated from the other members of the alkali group (1) by the ready solubility of its chloride in amyl alcohol (Gooch, Amer. Chem. Jour. ix, 33); (2) by the solvent action of absolute ethyl alcohol upon the chloride; (3) by the insolubility of the phosphate in the presence of ammonia and ethyl alcohol (Benedict, Amer. Chem. Jour. xxxii, 480); (4) by the comparative insolubility of the carbonate; (5) by the solubility of the fluosilicate (Reichard, Chem. Ztg. xxix, 861); (6) by the insolubility of

the sulphate in magnesium chloride formed by the addition of magnesium sulphate to mother liquors containing chlorides (Siebert, Pharm. Centr. XLVI, 368); (7) by the solubility of the chloride in pyridine (Kahlenberg, Jour. Amer. Chem. Soc. XXIV, 401).

### EXPERIMENTAL WORK ON LITHIUM.

*Experiment 1. Extraction of lithium salts from triphylite or lithiophilite.* Dissolve 25 to 50 grm. of finely powdered mineral in common hydrochloric acid, add sufficient nitric acid to oxidize the iron, and enough ferric chloride to combine with all the phosphoric acid present. Evaporate to dryness and extract with hot water. Treat the extract with barium hydroxide in slight excess. Filter, add sulphuric acid to complete precipitation of barium sulphate, and filter again. Convert the sulphates present into carbonates by the careful addition of barium carbonate, filter, acidify the filtrate with hydrochloric acid, evaporate to dryness, and extract the lithium chloride with alcohol.

(Lithium salts may be extracted also from the mother-liquor after the extraction of caesium and rubidium salts from lepidolite. The liquor is treated with barium carbonate in excess and is then boiled and filtered. The filtrate is acidified with hydrochloric acid, evaporated to dryness, and extracted with alcohol.)

*Experiment 2. Precipitation of lithium phosphate ( $\text{Li}_3\text{PO}_4$ ) and lithium fluoride ( $\text{LiF}$ ).* (a) To a solution of a lithium salt add sodium phosphate in solution. (b) Try similarly the action of sodium fluoride.

*Experiment 3. Precipitation of lithium carbonate ( $\text{Li}_2\text{CO}_3$ ).* To a few drops of a concentrated solution of a lithium salt add sodium carbonate in solution.

*Experiment 4. Solvent action of alcohol upon lithium salts.* Try the action of ethyl or amyl alcohol upon a little dry lithium nitrate or chloride.

*Experiment 5. Flame and spectroscopic tests for lithium.*

(a) Dip a platinum wire into a solution of a lithium salt and hold in a Bunsen flame. Note the color.

(b) Observe the lithium flame by means of the spectroscope. Note the bright crimson line between the potassium and sodium lines.

*Experiment 6. Negative tests of lithium salts.* Note that hydrogen sulphide, ammonium hydroxide, ammonium carbonate acting upon dilute solutions, chloroplatinic acid, and sodium cobaltic nitrite give no precipitate with lithium salts.

**RUBIDIUM, Rb, 85.45.**

**Discovery.** Rubidium was discovered by Bunsen and Kirchhoff in 1861, by means of the spectroscope, in the course of some work upon a lepidolite from Saxony (J. B. (1861), 173; Chem. News III, 357). The alkaline salts had been separated by the usual methods and precipitated with platinic chloride. The precipitate, when examined with the spectroscope, showed at first only the potassium lines. When it had been boiled repeatedly with water, however, the residue gave two violet lines situated between the strontium blue line and the potassium violet line at the extreme right of the spectrum. These increased in strength as the boiling continued, and with them appeared several other lines, among which were two almost coincident with the potassium red line ( $\alpha$ ) at the extreme left. These lines, observed for the first time, marked the discovery of an element; because of their color Bunsen gave it the name Rubidium, from the Latin *rubidus*, the deepest red.

**Occurrence.** Rubidium, like caesium, is widely distributed, but in very small quantities. It is found

(1) In minerals:

<i>Lepidolite</i> ,	$\text{R}_3\text{Al}(\text{SiO}_3)_3$ ,	contains 0.7–3.0% $\text{Rb}_2\text{O}$ .
<i>Leucite</i> ,	$\text{KAl}(\text{SiO}_3)_2$ ,	“ traces “
<i>Spodumene</i> ,	$\text{LiAl}(\text{SiO}_3)_2$ ,	“ “ “
<i>Triphylite</i> ,	$\text{Li}(\text{Fe}, \text{Mn})\text{PO}_4$ ,	“ “ “
<i>Lithiophilite</i> ,	$\text{Li}(\text{Mn}, \text{Fe})\text{PO}_4$ ,	“ “ “
<i>Carnallite</i> ,	$\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ ,	“ “ “
<i>Mica and orthoclase</i>		contain “ “

(2) In certain mineral waters, among which are the following: Ungemach, Ems, Kissingen, Nauheim, Selters, Vichy, Wildbad, Kochbrunnen (Wiesbaden), Dürkheim.

(3) In beet-root, many samples of tobacco, some coffee and tea, ash of oak and beech, crude cream of tartar, potashes, and mother-liquor from the Stassfurt potassium salt works.

**Extraction.** Rubidium may be extracted with caesium from lepidolite (*vid.* Extraction of Caesium).

**The Element.** *A. Preparation.* Elementary rubidium may be obtained (1) by heating the charred tartrates to a white heat (Bunsen); (2) by reducing the hydroxide or the carbonate with magnesium (Winkler, Ber. Dtsch. chem. Ges. xxiii, 51); (3) by reducing the hydroxide with aluminum (Beketoff); (4) by heating the chloride with calcium (*vid.* Lithium).

*B. Properties.* Rubidium is a soft white metal which melts at  $38^\circ \text{C}$ . It takes fire in the air, burning to the oxide. It decomposes water. Its specific gravity is 1.52.

**Compounds.** *A. Typical forms.* The following are typical compounds of rubidium:

Oxides,  $\text{Rb}_2\text{O}$ ;  $\text{Rb}_2\text{O}_2$ ;  $\text{Rb}_2\text{O}_3$ ;  $\text{Rb}_2\text{O}_4$ .

Hydroxide,  $\text{RbOH}$ .

Carbonates,  $\text{Rb}_2\text{CO}_3$ ;  $\text{RbHCO}_3$ .

Chloride,  $\text{RbCl}$ .

Double chlorides,  $\text{HgCl}_2 \cdot 2\text{RbCl}$ ;  $2\text{PbCl}_2 \cdot \text{RbCl}$ ;  $\text{BiCl}_3 \cdot 6\text{RbCl}$ ;

$\text{CdCl}_2 \cdot 2\text{RbCl}$ ;  $2\text{AsCl}_3 \cdot 3\text{RbCl}$ ;  $3\text{SbCl}_3 \cdot 5\text{RbCl}$ ;  
 $\text{MnCl}_2 \cdot 2\text{RbCl} + 2\text{H}_2\text{O}$ ;  $\text{ZnCl}_2 \cdot 2\text{RbCl}$ ;  $\text{MgCl}_2 \cdot \text{RbCl} + 6\text{H}_2\text{O}$ ;  
 $\text{AuCl}_3 \cdot \text{RbCl}$ ;  $\text{TeCl}_4 \cdot 2\text{RbCl}$ ;  $\text{TiCl}_3 \cdot 2\text{RbCl} + \text{H}_2\text{O}$ ;  
 and many others.

Chlorate,  $\text{RbClO}_3$ .

Perchlorate,  $\text{RbClO}_4$ .

Bromides,  $\text{RbBr}$ ;  $\text{RbBr}_3$ .

Double bromides,  $2\text{PbBr}_2 \cdot \text{RbBr}$ ;  $2\text{AsBr}_3 \cdot 3\text{RbBr}$ ;  $2\text{SbBr}_3 \cdot 3\text{RbBr}$ ;  
 $\text{AuBr}_3 \cdot \text{RbBr}$ ;  $\text{TeBr}_4 \cdot 2\text{RbBr}$ ;  $\text{TlBr}_3 \cdot 3\text{RbBr} + \text{H}_2\text{O}$ .

Iodides,  $\text{RbI}$ ;  $\text{RbI}_3$ ; and others.

Double iodides,  $\text{AgI} \cdot 2\text{RbI}$ ;  $\text{PbI}_2 \cdot \text{RbI} + 2\text{H}_2\text{O}$ ;  $2\text{AsI}_3 \cdot 3\text{RbI}$ ;  
 $2\text{SbI}_3 \cdot 3\text{RbI}$ ;  $\text{TeI}_4 \cdot 2\text{RbI}$ ;  $\text{TlI}_3 \cdot \text{RbI} + 2\text{H}_2\text{O}$ .

Iodates,  $\text{RbIO}_3$ ;  $\text{RbIO}_3 \cdot \text{HIO}_3$ ;  $\text{RbIO}_3 \cdot 2\text{HIO}_3$ .

Nitride,  $\text{RbN}_3$ .

Nitrates,  $\text{RbNO}_3$ ;  $3\text{RbNO}_3 \cdot \text{Co}(\text{NO}_3)_3 + \text{H}_2\text{O}$ .

Cyanide,  $\text{RbCN}$ .

Sulphates,  $\text{Rb}_2\text{SO}_4$ ;  $\text{RbHSO}_4$ ;  $\text{Rb}_2\text{S}_2\text{O}_7$ ;  $\text{Rb}_2\text{O} \cdot 8\text{SO}_3$ .

Alums,  $\text{RbAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ ;  $\text{RbFe}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ ;  
 $\text{RbCr}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ ;  $\text{Rb}_2\text{SO}_4 \cdot \text{Ti}_2\text{O}_3 \cdot 3\text{SO}_3 + 24\text{H}_2\text{O}$ .

Chloroplatinate,  $\text{Rb}_2\text{PtCl}_6$ .

Silicofluoride,  $\text{Rb}_2\text{SiF}_6$ .

*B. Characteristics.* The rubidium compounds are soluble, and similar to those of potassium and caesium (*vid.* Caesium). Among the important insoluble salts are the perchlorate ( $\text{RbClO}_4$ ), the silicofluoride ( $\text{Rb}_2\text{SiF}_6$ ), the chloroplatinate ( $\text{Rb}_2\text{PtCl}_6$ ), the bitartrate ( $\text{RbHO}_2\text{C}_4\text{H}_4\text{O}_4$ ), the alums ( $\text{RbAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$  and  $\text{RbFe}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ ), and the cobaltic nitrite ( $\text{Rb}_3\text{Co}(\text{NO}_2)_6$ , typical). The salts of rubidium color the flame violet. The spectrum gives two lines in the violet to the right of the caesium lines ( $\text{Rb}\alpha$  and  $\text{Rb}\beta$ ), also two lines not so distinct in the dark red ( $\text{Rb}\gamma$  and  $\text{Rb}\delta$ ), near the potassium red line, at the left of the spectrum.

**Estimation, Separation, and Experimental Work.** *Vid.* Caesium.

## CÆSIUM, Cs, 132.9.

**Discovery.** Cæsium was discovered in 1860 by Bunsen and Kirchhoff while they were engaged in the spectroscopic examination of a mother-liquor from the waters of Dürkheim spring (Pogg. Annal. cxiii, 337; Chem. News II, 281). After the removal of the strontium, calcium, and magnesium, by well-known methods, and of the lithium as far as possible by ammonium carbonate, the mother-liquor was tested, and gave, in addition to the potassium, sodium, and lithium lines, two beautiful blue lines never before observed, near the strontium blue lines. Bunsen gave the name Cæsium to the newly discovered element, from the Latin *caesius*, the blue of the clear sky.

**Occurrence.** Cæsium is found in combination as follows:

(1) In minerals:

*Pollucite*,  $H_2Cs_4Al_4(SiO_3)_8$ , contains 31–37%  $Cs_2O$ .

*Lepidolite*,  $LiK(Al(OH,F)_2) \cdot Al(SiO_3)_3$ , contains 0.2–0.7%  $Cs_2O$ .

*Beryl*,  $Be_3Al_2(SiO_3)_6$ , contains 0–3%  $Cs_2O$ .

(2) In certain mineral waters, among which are Dürkheim (1 liter contains about 0.21 mg.  $RbCl$  and 0.17 mg.  $CsCl$ ), Nauheim, Baden-Baden, Frankenhausen, Kreuznacher, Bourbonne les Bains, Monte Catino, Wheal Clifford.

**Extraction.** Of the methods in use for the extraction of cæsium the following may serve as examples:

(1) *From pollucite.* The finely powdered mineral is decomposed on a water-bath with strong hydrochloric acid. To the acid solution antimony trichloride is added, which precipitates the double chloride of antimony and cæsium ( $3CsCl \cdot 2SbCl_3$ ) (Wells, Amer. Chem. Jour. xxvi, 265).



Or the acid solution may be treated with a solution of lead chloride containing free chlorine. This precipitates a double chloride of caesium and tetravalent lead ( $2\text{CsCl} \cdot \text{PbCl}_4$ ) (Wells, Amer. Jour. Sci. [3] XLVI, 186).

(2) *From any silicate.* The mineral is heated with a mixture of calcium carbonate and ammonium chloride, and the fused mass is cooled and extracted with water. The liquid is then evaporated to a small volume, and sulphuric acid is added to precipitate the calcium as the sulphate. After filtration, evaporation is continued until the greater part of the hydrochloric acid has been expelled. Sodium or ammonium carbonate is then added to complete the removal of the calcium salt. Upon the addition of chloroplatinic acid the caesium and rubidium are precipitated as the salts of that acid. By the action of hydrogen upon these salts the platinum is precipitated, while the caesium and rubidium chlorides are left in solution.

(3) *From lepidolite.* The mineral is decomposed by heating with a mixture of calcium fluoride and sulphuric acid (*vid.* Experiment 1).

**The Element.** *A. Preparation.* Elementary caesium may be obtained (1) by heating caesium hydroxide with aluminum to redness in a nickel retort (Beketoff, Bull. Acad. Petersburg IV, 247); (2) by heating caesium hydroxide with magnesium in a current of hydrogen (Erdmann and Menke, Jour. Amer. Chem. Soc. XXI, 259, 420); (3) by heating caesium carbonate with magnesium in a current of hydrogen (Graefe and Eckardt, Zeitsch. anorg. Chem. XXII, 158); (4) by heating the chloride with calcium (*vid.* Lithium).

*B. Properties.* Caesium, the most positive of the metals, is silvery white and soft. It takes fire quickly in the air, burning to the oxide. It melts at  $26^\circ \text{C}$ . Like the other alkaline metals it decomposes water. Determinations of its specific gravity range from 1.88 to 2.4.

**Compounds.** *A. Typical forms.* The following are typical compounds of cæsium:

Oxides,  $\text{Cs}_2\text{O}$ ;  $\text{Cs}_2\text{O}_2$ ;  $\text{Cs}_2\text{O}_3$ ;  $\text{Cs}_2\text{O}_4$ .

Hydroxide,  $\text{CsOH}$ .

Carbonates,  $\text{Cs}_2\text{CO}_3$ ;  $\text{CsHCO}_3$ .

Chloride,  $\text{CsCl}$ .

Double chlorides,  $\text{AgCl} \cdot \text{CsCl}$ ;  $\text{HgCl}_2 \cdot \text{CsCl}$ ;  $\text{PbCl}_4 \cdot 2\text{CsCl}$ ;  $\text{PbCl}_2 \cdot 4\text{CsCl}$ ;  $2\text{BiCl}_3 \cdot 3\text{CsCl}$ ;  $\text{CuCl}_2 \cdot 2\text{CsCl}$ ;  $\text{Cu}_2\text{Cl}_2 \cdot \text{CsCl}$ ;  $\text{CdCl}_2 \cdot 2\text{CsCl}$ ;  $2\text{AsCl}_3 \cdot 3\text{CsCl}$ ;  $2\text{SbCl}_3 \cdot 3\text{CsCl}$ ;  $\text{SnCl}_2 \cdot \text{CsCl}$ ;  $\text{Fe}_2\text{Cl}_6 \cdot 6\text{CsCl}$ ;  $\text{CoCl}_2 \cdot 3\text{CsCl}$ ;  $\text{NiCl}_2 \cdot 2\text{CsCl}$ ;  $\text{MnCl}_2 \cdot 2\text{CsCl}$ ;  $\text{ZnCl}_2 \cdot 3\text{CsCl}$ ;  $\text{MgCl}_2 \cdot \text{CsCl} + 6\text{H}_2\text{O}$ ;  $\text{AuCl}_3 \cdot \text{CsCl}$ ;  $\text{PtCl}_4 \cdot 2\text{CsCl}$ ;  $\text{PtCl}_2 \cdot 2\text{CsCl}$ ;  $\text{PdCl}_2 \cdot 2\text{CsCl}$ ;  $\text{TeCl}_4 \cdot 2\text{CsCl}$ ;  $\text{TlCl}_3 \cdot 3\text{CsCl} + \text{H}_2\text{O}$ ; and many others.

Bromides,  $\text{CsBr}$ ;  $\text{CsBr}_3$ ;  $\text{CsBr}_5$ .

Double bromides,  $\text{HgBr}_2 \cdot \text{CsBr}$ ;  $\text{PbBr}_2 \cdot 4\text{CsBr}$ ;  $\text{CuBr}_2 \cdot 2\text{CsBr}$ ;  $\text{CdBr}_2 \cdot 3\text{CsBr}$ ;  $2\text{AsBr}_3 \cdot 3\text{CsBr}$ ;  $\text{CoBr}_2 \cdot 2\text{CsBr}$ ;  $\text{NiBr}_2 \cdot \text{CsBr}$ ;  $\text{ZnBr}_2 \cdot 2\text{CsBr}$ ;  $\text{MgBr}_2 \cdot \text{CsBr} + 6\text{H}_2\text{O}$ ;  $\text{AuBr}_3 \cdot \text{CsBr}$ ;  $\text{TeBr}_4 \cdot 2\text{CsBr}$ ;  $2\text{TlBr}_3 \cdot 3\text{CsBr}$ ; and many others.

Iodides,  $\text{CsI}$ ;  $\text{CsI}_3$ ;  $\text{CsI}_5$ .

Double iodides,  $\text{HgI}_2 \cdot \text{CsI}$ ;  $\text{PbI}_2 \cdot \text{CsI}$ ;  $\text{CdI}_2 \cdot 3\text{CsI}$ ;  $2\text{AsI}_3 \cdot 3\text{CsI}$ ;  $\text{CoI}_2 \cdot 2\text{CsI}$ ;  $\text{ZnI}_2 \cdot 3\text{CsI}$ ;  $\text{TeI}_4 \cdot 2\text{CsI}$ ;  $\text{TlI}_3 \cdot \text{CsI}$ ; and many others.

Mixed halides,  $\text{HgCs}_3\text{Cl}_3\text{Br}_2$ ;  $\text{HgCs}_2\text{Cl}_2\text{Br}_2$ ;  $\text{HgCsClBr}_2$ ;  $\text{Hg}_4\text{CsClBr}_{10}$ ;  $\text{HgCs}_3\text{Br}_3\text{I}_2$ ;  $\text{HgCs}_2\text{Br}_2\text{I}_2$ ;  $\text{HgCsBrI}_2$ ;  $\text{HgCs}_2\text{Cl}_2\text{I}_2$ ;  $\text{PbCs}_4(\text{ClBr})_6$ ;  $\text{PbCs}(\text{ClBr})_3$ ;  $\text{Pb}_2\text{Cs}(\text{ClBr})_5$ .

Double fluorides,  $2\text{CsF} \cdot \text{ZrF}_4$ ;  $\text{CsF} \cdot \text{ZrF}_4 + \text{H}_2\text{O}$ ;  $2\text{CsF} \cdot 3\text{ZrF}_4 + 2\text{H}_2\text{O}$ .

Iodates,  $\text{CsIO}_3$ ;  $2\text{CsIO}_3 \cdot \text{I}_2\text{O}_5$ ;  $2\text{CsIO}_3 \cdot \text{I}_2\text{O}_5 + 2\text{HIO}_3$ .

Nitride,  $\text{CsN}_3$  (Jour. Amer. Chem. Soc. xx, 225).

Nitrates,  $\text{CsNO}_3$ ;  $3\text{CsNO}_3 \cdot \text{Co}(\text{NO}_3)_3 + \text{H}_2\text{O}$ .

Sulphates,  $\text{Cs}_2\text{SO}_4$ ;  $\text{CsHSO}_4$ ;  $\text{Cs}_2\text{S}_2\text{O}_7$ ;  $\text{Cs}_2\text{O} \cdot 8\text{SO}_3$ .

Alums,  $\text{CsAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ ;  $\text{Cs}_2\text{SO}_4 \cdot \text{Mn}_2(\text{SO}_4)_3 + 24\text{H}_2\text{O}$ ;  $\text{Cs}_2\text{SO}_4 \cdot \text{Ti}_2\text{O}_3 \cdot 3\text{SO}_3 + 24\text{H}_2\text{O}$ .

Fluosilicate,  $\text{Cs}_2\text{SiF}_6$ .

Chromates,  $\text{Cs}_2\text{CrO}_4$ ;  $\text{Cs}_2\text{Cr}_2\text{O}_7$ .

Chloroplatinate,  $\text{Cs}_2\text{PtCl}_6$ .

Cobaltic nitrite,  $\text{Cs}_3\text{Co}(\text{NO}_2)_6$ ,\* typical.

*B. Characteristics.* With few exceptions the caesium compounds are soluble in water. They closely resemble the potassium and rubidium compounds, being for the most part isomorphous with them. A comparison of the solubilities of the alums and also of the chloroplatinates of the three elements, at a temperature of  $15^\circ$ – $17^\circ$  C., follows:

100 parts of water will dissolve

$\text{CsAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ , 0.62 parts;  $\text{Cs}_2\text{PtCl}_6$ , 0.18 parts.

$\text{RbAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ , 2.30 “  $\text{Rb}_2\text{PtCl}_6$ , 0.20 “

$\text{KAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ , 13.50 “  $\text{K}_2\text{PtCl}_6$ , 2.17 “

Among the important insoluble salts are the chloroplatinate ( $\text{Cs}_2\text{PtCl}_6$ ), the alum ( $\text{CsAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ ), the cobaltic nitrite ( $\text{Cs}_3\text{Co}(\text{NO}_2)_6$ , typical), and the double chlorides with tetravalent lead ( $\text{PbCl}_4 \cdot 2\text{CsCl}$ ), tetravalent tin ( $2\text{CsCl} \cdot \text{SnCl}_4$ ?), and trivalent antimony ( $3\text{CsCl} \cdot 2\text{SbCl}_3$ ). The salts of caesium color the flame violet. The spectrum shows two sharply defined lines in the blue, designated on the scale as  $\text{Cs}\alpha$  and  $\text{Cs}\beta$ .

**Estimation of Caesium and Rubidium.** Caesium and rubidium may be estimated in general by the methods applied to potassium. They are usually weighed as the normal sulphates, after evaporation of suitable salts with sulphuric acid and ignition of the products; other methods, however,

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\* Cs may be partly replaced by Na.

such as the chloroplatinate and chloride methods, are possible. They may be weighed with a fair degree of accuracy as the acid sulphates, after evaporation with an excess of sulphuric acid, and heating at  $250^{\circ}$ – $270^{\circ}$  C. until a constant weight is obtained (Browning, Amer. Jour. Sci. [4] XII, 301). They may also be estimated by precipitation with sodium cobaltic nitrite, decomposition of the cobaltic nitrites with hydrochloric acid, and precipitation of the perchlorates by a 30% perchloric acid solution (Montemartini, Gaz. chim. ital. XXXIII (II), 189; Chem. Zentr. 1904 (I), 119). Rubidium may be estimated by means of the spectroscope by comparing the intensity of the spectrum lines obtained from a definite amount of solution of rubidium salt to be estimated with that of the lines obtained from a definite amount of a solution of known strength (Gooch and Phinney, Amer. Jour. Sci. [3] XLIV, 392).

**Separation of Cæsium and Rubidium.** These metals belong to the alkali group. From sodium and lithium they may be separated (1) by chloroplatinic acid, with which they form insoluble salts; and (2) by aluminum sulphate, with which they form difficultly soluble alums. From potassium they may be separated by the greater solubility of the potassium alum and chloroplatinate in water.

Cæsium and rubidium may be separated from each other (1) by the difference in solubility of the chloroplatinates; \* (2) by the difference in solubility of the alums; \* (3) by the formation of the more stable and less soluble tartrate of rubidium; and (4) by the solubility of cæsium carbonate in absolute alcohol. Probably the most satisfactory methods, however, are those suggested by Wells; they depend upon the insolubility of the following salts: cæsium double chloride and iodide ( $\text{CsCl}_2\text{I}$ ) (Amer. Jour.

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\* *Vid.* p. 12.

Sci. [3] XLIII, 17), caesium-lead chloride ( $\text{Cs}_2\text{PbCl}_4$ ) (ibid. [3] XLVI, 186), and caesium-antimony chloride ( $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ ) (Amer. Chem. Jour. xxvi, 265).

### EXPERIMENTAL WORK ON CAESIUM AND RUBIDIUM.

*Experiment 1. Extraction of caesium and rubidium salts from lepidolite.* Mix thoroughly in a lead or platinum dish 100 grm. of finely ground lepidolite with an equal amount of powdered fluorspar. Add 50 cm.<sup>3</sup> of common sulphuric acid and stir until the mass has the consistency of a thin paste. Set aside in a draught hood until the first evolution of fumes ( $\text{SiF}_4$  and  $\text{HF}$ ) has nearly ceased. Heat on a plate or sand-bath at a temperature of  $200^\circ$ – $300^\circ$  C. until the mass is dry and hard. Pulverize and extract with hot water until the washings give no precipitate on the addition of ammonium hydroxide to a few drops. Evaporate the entire solution to about 100 cm.<sup>3</sup> and filter while hot to remove the calcium sulphate. Set the clear filtrate aside to crystallize. The crystals, consisting of a mixture of potassium, caesium, and rubidium alums, with some lithium salt, should be dissolved in about 100 cm.<sup>3</sup> of distilled water, and allowed to recrystallize. This process of recrystallization should be repeated until the crystals give no test before the spectroscope for either lithium or potassium. The amount of caesium and rubidium alums obtained will of course vary with the variety of lepidolite used. An average amount of the mixed alums of potassium, caesium, and rubidium from the first crystallization would be 10 grm. The pure caesium and rubidium alums finally obtained should be about 3 grm. (Robinson and Hutchins, Amer. Chem. Jour. vi, 74). Lithium may be extracted from the mother-liquor (*vid.* Experiment 1, Lithium).

*Experiment 2. Preparation of cæsium and rubidium sulphates* ( $\text{Cs}_2\text{SO}_4$ ;  $\text{Rb}_2\text{SO}_4$ ). Dissolve in water a crystal of the cæsium and rubidium alums obtained from lepidolite, add a few drops of ammonium hydroxide, and boil. Filter off the aluminum hydroxide and evaporate the filtrate to dryness. Ignite until the ammonium sulphate is removed, dissolve in a few drops of water, filter, and evaporate to dryness. Sulphates of cæsium and rubidium will remain.

*Experiment 3. Preparation of the carbonates of cæsium and rubidium* ( $\text{Cs}_2\text{CO}_3$ ;  $\text{Rb}_2\text{CO}_3$ ). Dissolve in water a crystal of cæsium and rubidium alums obtained from lepidolite, add an excess of barium carbonate, and boil. Filter off the alumina, barium sulphate, and excess of barium carbonate. Pass a little carbon dioxide through the clear filtrate and boil to remove traces of barium salt. Filter. Carbonates of cæsium and rubidium will remain in solution.

*Experiment 4. Formation of the double chloride of cæsium and tetravalent lead* ( $2\text{CsCl} \cdot \text{PbCl}_4$ ). To a few cm.<sup>3</sup> of a one per cent. solution of a cæsium salt add a few drops of the reagent obtained by warming lead dioxide with hydrochloric acid and allowing the solution to stand until cool. Make a similar experiment, using a rubidium salt in place of the cæsium salt. Note the absence of precipitation in this case.

*Experiment 5. Precipitation of the double chloride of cæsium and antimony* ( $3\text{CsCl} \cdot 2\text{SbCl}_3$ ). To a few cm.<sup>3</sup> of a one per cent. solution of a cæsium salt add some antimony trichloride in solution and evaporate to a small volume. The double chloride will be precipitated on cooling. Repeat the experiment, using a rubidium salt. Note the absence of precipitation in this case.

*Experiment 6. Precipitation of the double salt cæsium chloride and stannic chloride* ( $2\text{CsCl} \cdot \text{SnCl}_4$ ). Make an ex-

periment similar to Experiment 5, using stannic chloride in the place of antimonious chloride. Note the separation of the double chloride on cooling. Make a similar experiment, using a rubidium salt.

*Experiment 7. Precipitation of the chloroplatinates of cæsium and rubidium* ( $\text{Cs}_2\text{PtCl}_6$ ;  $\text{Rb}_2\text{PtCl}_6$ ). To a few cm.<sup>3</sup> of a solution of a cæsium salt add a few drops of a solution of chloroplatinic acid. Make a similar experiment with a solution of a rubidium salt.

*Experiment 8. Precipitation of the cobaltic nitrites of cæsium and rubidium.* Try the action of a solution of sodium cobaltic nitrite upon separate solutions of cæsium and rubidium salts.

*Experiment 9. Flame tests for cæsium and rubidium.* Dip the end of a platinum wire into a solution of a cæsium salt and test the action of the flame of a Bunsen burner upon it. Repeat, using a rubidium salt.

*Experiment 10. Spectroscopic tests for cæsium and rubidium.* Test solutions of cæsium and rubidium salts before the spectroscope. Note the twin blue lines of the cæsium spectrum and the twin violet lines of the rubidium.

*Experiment 11. Negative tests of cæsium and rubidium.* Note that hydrogen sulphide, ammonium sulphide, and ammonium carbonate give no precipitates with salts of cæsium and rubidium.

## CHAPTER II.

### BERYLLIUM, Be, 9.1.

**Discovery.** In the year 1797, Vauquelin discovered beryllium or glucinum in the mineral beryl (Ann. de Chim. xxvi, 155). After having removed the silica in the usual manner, he precipitated with carbonate of potassium, and treated the precipitate with a solution of caustic potash. The greater part of the precipitate dissolved, leaving a residue which he found to consist of a small amount of iron oxide and an oxide which dissolved in sulphuric acid. This solution gave, on evaporation, irregular crystals having a sweetish taste and forming no alum with potassium sulphate. In his early articles Vauquelin refers to the oxide as "la terre du Béril," which the German chemists translated, "Berylerde." The sweet taste suggested for the new element the name Glucinum, from *γλυκίς*, *sweet*. The name Beryllium, from the chief source, beryl, has been more generally used.

**Occurrence.** Beryllium occurs in minerals as follows:

<i>Beryl</i> ,	$\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ ,	contains 11-15% BeO.
<i>Chrysoberyl</i> ,	$\text{BeAl}_2\text{O}_4$ ,	" 19-20% "
<i>Bertrandite</i> ,	$\text{Be}_2(\text{Be} \cdot \text{OH})_2\text{Si}_2\text{O}_7$ ,	" 40-43% "
<i>Phenacite</i> ,	$\text{Be}_2\text{SiO}_4$ ,	" 44-46% "
<i>Leucophanite</i> ,	$\text{Na}(\text{BeF})\text{Ca}(\text{SiO}_3)_2$ ,	" 10-12% "
<i>Meliphanite</i> ,	$\text{NaCa}_2\text{Be}_2\text{FSi}_3\text{O}_{10}$	" 10-14% "
<i>Epididymite</i> ,	$\text{HNaBeSi}_3\text{O}_8$ ,	" 10-11% "
<i>Euclase</i> ,	$\text{Be}(\text{Al} \cdot \text{OH})\text{SiO}_4$ ,	" 17-18% "
<i>Helvite</i> or <i>danalite</i> ,	$\overset{\text{II}}{\text{R}}_5(\overset{\text{II}}{\text{R}}_2\text{S})(\text{SiO}_4)_3$ ,	" 13-14% "



<i>Gadolinite</i> ,	$\text{FeBe}_2\text{Y}_2\text{Si}_2\text{O}_{10}$ ,	contains	5-11%	BeO.
<i>Trimerite</i> ,	$\text{Be}(\text{Mn}, \text{Ca}, \text{Fe})\text{SiO}_4$ ,	"	16-17%	"
<i>Cyrtolite</i> ,	complex silicate,	"	14-15%	"
<i>Alvite</i> ,	" "	"	circa 14%	"
<i>Allanite</i> ,	" "	"	0-3%	"
<i>Muromonite</i> ,	" "	"	5-6%	"
<i>Erdmanite</i> ,	" "	"	0-4%	"
<i>Foresite</i> ,	" "	"	0-1%	"
<i>Arrhenite</i> ,	complex silico-tantalate,	"	circa 1%	"
<i>Beryllionite</i> ,	$\text{NaBePO}_4$ ,	"	19-20%	"
<i>Herderite</i> ,	$\text{Ca}(\text{Be}(\text{OH}, \text{F}))\text{PO}_4$ ,	"	15-16%	"
<i>Hambergite</i> ,	$\text{Be}(\text{BeOH})\text{BO}_3$ ,	"	53-54%	"
<i>Sipylite</i> ,	$\text{ErNbO}_4$ .	"	circa .6%	"
<i>Tengerite</i> ,	complex carbonate,	"	9-10%	"

Beryllium is found also in traces in some monazite sands and aluminous schists, and in some mineral waters.

**Extraction.** Beryllium is generally extracted from beryl by one of the following methods:

(1) The mineral is fused with sodium or potassium hydroxide (*vid.* Experiment 1).

(2) The finely ground mineral is fused with three times its weight of potassium fluoride. The fused mass is treated with strong sulphuric acid and warmed; by this process the silica is removed as silicon fluoride, and the alumina and potash are united to form the alum, which may be crystallized out on evaporation. The beryllium remains in solution as the sulphate, and may be removed by the treatment described in Experiment 1.

(3) The mineral is fused with calcium fluoride. This process is in general the same as the one indicated in the second method, except that calcium sulphate is formed and must be removed (Lebeau, *Chem. News* LXXIII, 3).

(4) The mineral is decomposed by fusion (a) with

sodium and potassium carbonates, or (b) with acid potassium sulphate.

**The Element.** *A. Preparation.* Elementary beryllium may be obtained (1) by bringing together the vapor of the chloride and sodium in a current of hydrogen (Debray, Ann. Chim. Phys. (1855) XLIV, 5); (2) by fusing the chloride with potassium (Wöhler, Pogg. Annal. XIII, 577); (3) by heating the chloride in a closed iron crucible with sodium (Nilson and Pettersson, Ber. Dtsch. chem. Ges. XI, 381, 906); (4) by electrolyzing the double fluoride of beryllium and sodium or potassium (Lebeau); (5) by heating the chloride in a bomb with sodium (Hunter).

*B. Properties.* The element beryllium is dark steel-gray in color. At ordinary temperatures unchanged in air and in oxygen, it burns brightly to the oxide when heated in either. It does not decompose hot or cold water. When heated it combines readily with fluorine, chlorine, bromine and iodine. It is soluble in dilute and in concentrated acids; also in potassium hydroxide with the liberation of hydrogen. Determinations of its specific gravity range from 1.75 to 1.85.

Alloys of beryllium with many of the common metals are known, as are also alloys with chromium, molybdenum and tungsten (Lebeau). An alloy of copper and beryllium containing from .5% to 1.3% beryllium is very sonorous.

**Compounds.** *A. Typical forms.* The following are typical compounds of beryllium:

*Fluorides,*  $\text{BeF}_2$ ;  $\text{BeF}_{2.2}\text{NaF}$ ;  $\text{BeF}_{2.2}\text{KF}$ ;  $\text{BeF}_{2.2}\text{NH}_4\text{F}$ .

*Chlorides,*  $\text{BeCl}_2$ ;  $\text{BeCl}_{2.2}\text{AuCl}_3$ ;  $\text{BeCl}_{2.2}\text{FeCl}_3 \cdot \text{H}_2\text{O}$ ;  $\text{BeCl}_{2.2}\text{CrCl}_3 \cdot \text{H}_2\text{O}$ ;  $3\text{BeCl}_{2.2}\text{Ti}_2\text{Cl}_6$ ;  $\text{BeCl}_{2.2}\text{ICl}_3 \cdot 8\text{H}_2\text{O}$ ;  $\text{BeCl}_{2.2}\text{PtCl}_4 \cdot 8\text{H}_2\text{O}$ ;  $\text{BeCl}_{2.2}\text{PdCl}_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{BeCl}_{2.2}\text{PdCl}_4 \cdot 8\text{H}_2\text{O}$ .

*Bromide,*  $\text{BeBr}_2$ .

*Iodide,*  $\text{BeI}_2$ .

*Hydroxide*,  $\text{Be}(\text{OH})_2$ .

*Oxide*,  $\text{BeO}$ .

*Sulphide*,  $\text{BeS}$ .

*Cyanides*,  $\text{BePt}(\text{CN})_{4.4}\text{H}_2\text{O}$ ;  $\text{BeMg}_2\text{Pt}_3(\text{CN})_{12}$ ;  $\text{BePtBr}_2(\text{CN})_4$ .

*Carbides*,  $\text{Be}_2\text{C}$ ;  $3\text{Be}_2\text{C}.\text{B}_6\text{C}$ .

*Sulphates*,  $\text{BeSO}_4$ ;  $\text{BeSO}_4.2\text{H}_2\text{O}$ ;  $\text{BeSO}_4.4\text{H}_2\text{O}$ ;  $\text{BeSO}_4.\text{K}_2\text{SO}_4.2\text{H}_2\text{O}$ ;  $\text{BeSO}_4.\text{K}_2\text{SO}_4.\text{KHSO}_4.4\text{H}_2\text{O}$ ;  $3\text{BeSO}_4.2\text{Na}_2\text{SO}_4.12\text{H}_2\text{O}$ ;  $\text{BeSO}_4.(\text{NH}_4)_2\text{SO}_4.2\text{H}_2\text{O}$ .

*Sulphites*,  $\text{BeSO}_3.\text{H}_2\text{O}$ ;  $\text{BeSO}_3.2\text{H}_2\text{O}$ ;  $2\text{BeSO}_3.\text{K}_2\text{SO}_3.9\text{H}_2\text{O}$ ;  $2\text{BeSO}_3.(\text{NH}_4)_2\text{SO}_3.4\text{H}_2\text{O}$ .

*Selenate*,  $\text{BeSeO}_4.4\text{H}_2\text{O}$ .

*Selenites*,  $\text{BeSeO}_3.\text{H}_2\text{O}$ ;  $\text{BeSeO}_3.2\text{H}_2\text{O}$ .

*Nitrate*,  $\text{Be}(\text{NO}_3)_{2.4}\text{H}_2\text{O}$ .

*Phosphates*,  $\text{BeHPO}_4.3\text{H}_2\text{O}$ ;  $\text{BeKPO}_4$ ;  $\text{BeNaPO}_4$ ;  $\text{BeNa}_2(\text{NH}_4)_2(\text{PO}_4)_2$ .

*Antimonate*,  $\text{Be}(\text{SbO}_3)_2.6\text{H}_2\text{O}$ .

*Carbonate*,  $x\text{BeCO}_3.y\text{Be}(\text{OH})_2$ .

*Silicates*,  $\text{BeSiO}_3$ ;  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ .

*Aluminate*,  $\text{Be}(\text{AlO}_2)_2$ .

*Methyl*,  $\text{Be}(\text{CH}_3)_2$ .

*Ethyl*,  $\text{Be}(\text{C}_2\text{H}_5)_2$ .

*Propyl*,  $\text{Be}(\text{C}_3\text{H}_7)_2$ .

*Acetates*,  $\text{Be}(\text{C}_2\text{H}_3\text{O}_2)_2$ ;  $\text{Be}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$ .

*Acetylacetonate*,  $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$ .

*Oxalates*,  $\text{BeC}_2\text{O}_4.3\text{H}_2\text{O}$ ;  $\text{BeC}_2\text{O}_4.\text{K}_2\text{C}_2\text{O}_4$ ; etc.

*Tartrates*,  $\text{BeC}_4\text{H}_4\text{O}_6.3\text{H}_2\text{O}$ ;  $\text{KBeC}_4\text{H}_3\text{O}_6$ ;  $\text{K}_2\text{Be}_4\text{C}_8\text{H}_4\text{O}_{13}.7\text{H}_2\text{O}$ ;  $\text{Na}_2\text{Be}_4\text{C}_8\text{H}_4\text{O}_{13}.10\text{H}_2\text{O}$ .

and many salts of organic acids; e. g., succinates, racemates, malates, formates, propionates, butyrates, trichloracetate (Parsons and Sargent, Jour. Amer. Chem. Soc. xxxi, 1202).

*B. Characteristics.* The compounds of beryllium closely resemble those of aluminum. The oxide is white; it is insoluble in water and unaffected by it. The hydroxide is

soluble in concentrated solutions of its own salts and is precipitated from them by dilution. It is also soluble in the alkali hydroxides and bicarbonates, and in dilute acids. The halides are very readily hydrolyzed by water, the hydrolysis in the case of the chlorides, bromides, and iodides being practically complete. Normal salts of the non-volatile acids only can be crystallized from water; of these the sulphate, oxalate, and selenate are examples. The nitrate can be prepared only by crystallization from strong nitric acid.

The double alkali tartrates are of peculiar interest, both on account of the fact that beryllium appears to replace not only the positive hydrogen of the acid but also in part the hydrogen of the tartrate ion, and also because the presence of beryllium in the salt increases the molecular rotation. This influence upon the molecular rotation is shown to an even greater degree in the case of the malates (Rosenheim and Itsig). Another interesting compound is the basic acetate, which, although almost insoluble in water, becomes soluble after hydrolysis by hot or cold water. It is soluble without decomposition in glacial acetic acid, methyl, ethyl, and amyl alcohols, chloroform, turpentine, ether acetone, carbon disulphide, and some other organic solvents. It is unaffected by dry air, melts at  $283^{\circ}$ – $284^{\circ}$  C., boils at  $330^{\circ}$ – $331^{\circ}$  C., and may be sublimed. It was used by Parsons in determining the atomic weight of beryllium. It is best prepared by the action of glacial acetic acid upon the dry carbonate or hydroxide. The chloride, nitrate and sulphate are the common soluble salts, and the nitrate and chloride are soluble in alcohol.

The arc spectrum of beryllium is characterized by lines in the blue and indigo.

**Estimation.** Beryllium is ordinarily estimated as the oxide, (BeO), which is obtained by the ignition of the precipitated hydroxide.

**Separation.** Beryllium closely resembles aluminum in many reactions. It may be separated from aluminum (1) by the action of a saturated solution of acid sodium carbonate upon the hydroxides of iron, aluminum and beryllium, beryllium hydroxide being dissolved (Parsons and Barnes); (2) by saturation of a solution of the two chlorides with hydrochloric acid gas in the presence of ether, the beryllium remaining in solution, while the aluminum chloride is precipitated (Gooch and Havens, Amer. Jour. Sci. [4] 11, 416); (3) by the action of hot glacial acetic acid upon the acetates, basic beryllium acetate separating out on cooling (Parsons and Robinson); by dehydration of the nitrates with amyl alcohol, the beryllium nitrate dissolving (Browning and Kuzirian).

## EXPERIMENTAL WORK ON BERYLLIUM.

*Experiment 1. Extraction of beryllium salts from beryl* ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ ). Fuse in a nickel or iron crucible 10 grm. of finely powdered mineral with 10 grm. of potassium hydroxide, and cool. Pulverize the fused mass, add water enough to cover it, and strong sulphuric acid in slight excess. Heat the gelatinous mass until fumes of sulphuric acid are given off and the residue has the appearance of a fine white powder. Extract thoroughly with hot water, discarding the insoluble material. Evaporate until the alums begin to crystallize from the solution, and allow to stand, when the greater part of the aluminum will separate as the alum. Treat the mother liquor from the alum with nitric acid, to convert all iron present to the ferric condition, neutralize with ammonium hydroxide, and add sodium acid carbonate in crystals to saturation, warming gently ( $50^\circ \text{C.}$ ), with frequent stirring for about an hour; or, if the quantity of hydroxide is small, bring rapidly to boiling and boil for one minute only. Filter, add a little ammonium sulphide to

remove any iron in solution, and dilute with about five or ten volumes of water. Pass steam through the liquid, or boil if the amount of beryllium is small, to precipitate the basic carbonate of beryllium (Parsons).

*Experiment 2. Precipitation of beryllium hydroxide* ( $\text{Be}(\text{OH})_2$ ). (a) To a solution of a beryllium salt add ammonium hydroxide, and note the insolubility of the precipitate in excess of that reagent.

(b) To another portion of the beryllium solution add a solution of potassium or sodium hydroxide, and note the solvent action of an excess.

(c) Dilute with water a portion of the alkaline solution obtained in (b) and boil. Note the reprecipitation of the hydroxide.

(d) To another portion of the alkaline solution obtained in (b) add ammonium chloride, and boil.

(e) To a solution of a beryllium salt add ammonium sulphide.

*Experiment 3. Precipitation of basic beryllium carbonate* ( $x\text{BeCO}_3.y\text{Be}(\text{OH})_2$ ). (a) To a solution of a beryllium salt add sodium or potassium carbonate in solution. Note the solvent action of an excess and the reprecipitation on boiling.

(b) Make a similar experiment, using ammonium carbonate.

*Experiment 4. Precipitation of beryllium phosphate* ( $\text{Be}_3(\text{PO}_4)_2$ ). To a solution of a beryllium salt add a solution of sodium phosphate.

*Experiment 5. Preparation of beryllium basic acetate* ( $\text{Be}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$ ). Dissolve some beryllium hydroxide or carbonate in acetic acid and evaporate to dryness. Dissolve the dry residue in excess of hot glacial acetic acid and allow the solution to cool.

*Experiment 6. Action of sodium acid carbonate upon beryllium hydroxide.* To a small amount of washed beryl-

lium hydroxide add 2-3 grm. of solid sodium acid carbonate and 20 cm.<sup>3</sup> of water, and heat rapidly to boiling. Note the solubility of the hydroxide. Dilute to 200 cm.<sup>3</sup> and boil. Note the precipitation of the hydroxide.

*Experiment 7. Solubility of beryllium salts in amyl alcohol.* To a few drops of a solution of beryllium chloride or nitrate add 5 cm.<sup>3</sup> of amyl alcohol and bring to the boiling point of the alcohol. Note the solubility of the salts in the alcohol.

*Experiment 8. Negative tests of beryllium salts.* Try the action of hydrogen sulphide and ammonium oxalate upon separate portions of a solution of a beryllium salt. Add sodium acetate to a solution of a beryllium salt and boil. Note the absence of precipitation in each case.

## CHAPTER III

### THE RADIO-ELEMENTS.\*

THE property of matter known as radioactivity was discovered in 1896 by M. Henri Becquerel, who observed that the salts of uranium emitted a characteristic radiation which was capable of producing an effect on a photographic plate through several thicknesses of black paper wholly opaque to ordinary light.

The radiation emitted by radioactive substances has been shown to be complex in character and to include three distinctive types known as the  $\alpha$ ,  $\beta$  and  $\gamma$  radiations.

The  $\alpha$  radiation consists of positively electrified atoms of helium moving with a velocity equal to about 1-15 of the velocity of light. The  $\alpha$  rays are completely stopped by thin layers of ordinary matter and are deflected by strong magnetic and electrostatic fields.

The  $\beta$  radiation consists of negatively electrified particles having a mass about one eighteen-hundredth that of a hydrogen atom and projected at a velocity which in some cases is as high as nine-tenths the velocity of light. The  $\beta$  rays have a greater power for penetrating matter than the  $\alpha$  rays, but are more readily deflected than the latter by both magnetic and electrostatic fields.

The  $\gamma$  radiation is believed to consist of ether pulses travelling with the velocity of light, and analogous in many

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\* This chapter was contributed by Bertram B. Boltwood, Ph.D., of Yale University.



respects to the Roentgen or X radiation. The  $\gamma$  rays have a high penetrative power and are not affected by either electrostatic or magnetic fields.

All three types of radiation are capable of producing charged carriers of electricity, known as ions, in the gases which they traverse, and in this manner render the gases conductive to electricity. They also excite phosphorescence in various chemical compounds and produce an effect on photographic plates.

The chemical elements which exhibit the phenomena of radioactivity are termed radio-elements. In order to explain their behavior, a theory, known as the disintegration theory, was proposed in 1902 by Rutherford and Soddy and has now been generally accepted. In this theory it is assumed that the radio-elements represent unstable forms of matter the atoms of which are spontaneously undergoing changes which result in the production of new forms of matter having different physical and chemical properties. These changes are accompanied by the emission of energy usually appearing in the form of heat derived from the internal energy of the atoms in process of transformation. The disintegration of the radio-elements takes place according to a simple exponential law which is given by the expression  $N = N_0 e^{-\lambda t}$ , where  $N_0$  is the number of atoms of the element present at the start,  $N$  is the number remaining unchanged after any time  $t$ ,  $e$  is the base of the natural system of logarithms and  $\lambda$  is the constant of change of the given element. The constant of change is a definite and characteristic quantity for any particular radio-element and its value is unaffected by any of the extremes of temperature and pressure to which it has been possible to subject radioactive substances. The constant of change represents the fraction of any given quantity of the radio-element which undergoes transformation in the unit of time.

The disintegration of the radio-elements is wholly inde-

pendent of the chemical state or form of combination of the radio-elements, and proceeds at a constant rate which is the same in all compounds of the same element. As a necessary consequence of this fact the relative radioactivity of different chemical compounds of the same radio-element is directly proportional to the relative quantities of the element which they each contain.

The instability of atomic structure may continue through a considerable number of successive changes until a final stable form of matter is reached. A radio-element from which any other radio-element is formed is called the "parent" of the latter and the element formed is known as the "product" of the parent from which it is produced.

The known radio-elements can be divided into two general groups: the uranium series and the thorium series. The uranium series comprises uranium and sixteen products of uranium, including ionium, radium, actinium, and polonium. The thorium series contains ten members in addition to thorium itself. The chemical behavior of the radio-elements, with the exception of uranium and thorium, has not been very thoroughly investigated, but there is every reason for believing that they all possess distinct and characteristic chemical properties.

### URANIUM, U, 238.5.

The general properties of uranium will be discussed on page 137. It is one of the most slowly changing of the radio-elements, its rate of disintegration corresponding to the transformation in one year of about one ten-billionth of the total amount of uranium present. The time required for exactly one-half of any given quantity of uranium to disintegrate completely into other forms of matter is about six billion years. Uranium when completely freed from its dis-

integration products emits only  $\alpha$  rays, but unless freshly prepared its compounds contain uranium X, which is the source of both a  $\beta$  and a  $\gamma$  radiation. Uranium salts can be obtained free from uranium X by recrystallization, the uranium X remaining in the mother liquor.

**Uranium X.** Uranium X is the first disintegration product of uranium and is gradually formed in uranium salts on standing. The amount which accumulates reached a maximum after about 150 days, when a state of radioactive equilibrium is reached and the amount of uranium X which is produced in any subsequent time is exactly equal to the amount which disintegrates in the same period. Uranium X was first discovered by Crookes in 1900. It emits  $\beta$  and  $\gamma$  rays, and in 24 days one-half of any given quantity of it is transformed into other substances. It can be obtained free from uranium by treating pure uranium nitrate, dried at  $118^\circ$ , with ordinary ether. The uranium nitrate is dissolved by the ether, leaving a slight residue which contains the greater part of the uranium X.

### IONIUM, Io.

Ionium is a radio-element intermediate between uranium, of which it is a product, and radium, of which it is the parent. It was discovered by Boltwood in 1907. It has not been obtained in sufficient quantity to permit a determination of its atomic weight or of its spectrum. From theoretical considerations its atomic weight is probably about 230. From uranium minerals containing thorium the ionium is separated with the thorium, to which it shows a striking similarity in chemical behavior. The constant of change of ionium has not yet been determined, but its rate of transformation is very possibly as slow as that of radium.

**RADIUM, Ra, 226.5.**

**Discovery.** Radium was discovered in 1898 by P. and S. Curie and G. Bemont. In the course of an investigation of the relative radioactivity of certain uranium salts and uranium minerals it was noted by Mme. Curie that although the activity of the uranium salts was quite closely proportional to the amounts of uranium contained in them, the activity of the uranium minerals was much greater than was to be expected from the uranium which they contained. This suggested that there might be present in the minerals some other more strongly radioactive constituent, and a further investigation led to the isolation of a highly radioactive substance resembling barium in its chemical properties.

**Occurrence.** Radium has been found widely distributed in minute proportions in many rocks and minerals, in sea water and in the waters of certain mineral springs. The chief source of radium has been the minerals containing a high proportion of uranium, principally pitchblende, and the present supply has been almost entirely obtained from the insoluble residues remaining after the treatment of pitchblende for the commercial extraction of uranium.

**Extraction.** The pitchblende residues consist chiefly of the sulphates of lead and calcium, together with the oxides of silicon, aluminum and iron. They also contain greater or less quantities of nearly all the metals (copper, bismuth, zinc, cobalt, manganese, nickel, vanadium, antimony, thallium, the rare earths, niobium, tantalum, arsenic, barium, etc.). They are first treated with boiling, concentrated sodium hydroxide solution, washed with water, and digested with hydrochloric acid. Much of the material is removed in this operation, the radium remaining in the undissolved portion. After further washing, the residue is boiled with a concentrated sodium carbonate solution which

converts the alkali-earths into carbonates. The residue is again washed to remove all traces of sulphates, and is then treated with hydrochloric acid, which dissolves the barium and radium together with certain of the other constituents. The solution of the chlorides is further purified until a salt containing only barium and radium is obtained. The mixed chlorides of barium and radium are subjected to a long series of fractional recrystallizations, the radium being concentrated in the least soluble portion of the fractions. In this manner a pure chloride of radium is ultimately obtained. The concentration of the radium proceeds more rapidly if the recrystallization is conducted with the double bromide.

**The Element.** By the electrolysis of a solution of radium chloride with a mercury cathode, S. Curie and Debierne in 1910 obtained radium amalgam which on distillation in hydrogen left a residue of metallic radium. It is a white metal melting at about  $700^{\circ}$ . It alters rapidly in the air with the formation of nitride and decomposes water with the formation of the hydroxide.

**Compounds.** *A. Typical forms.* The following compounds of radium have been described:

Hydroxide, $\text{Ra}(\text{OH})_2$ .	Chloride, $\text{RaCl}_2$ ; $\text{RaCl}_2 \cdot 2\text{H}_2\text{O}$ .
Carbonate, $\text{RaCO}_3$ .	Bromide, $\text{RaBr}_2$ ; $\text{RaBr}_2 \cdot 2\text{H}_2\text{O}$ .
	Nitrate, $\text{Ra}(\text{NO}_3)_2$ .

*B. Characteristics.* The exceeding rarity of the compounds of radium has rendered impossible any extensive study of their chemical characteristics. Their behavior, however, is very similar to that of the barium compounds. The chloride is described as a grayish-white powder, less soluble in water and in dilute hydrochloric acid than is the chloride of barium. The bromide gives off bromine in the air, and becomes alkaline because of the formation of the hydroxide. The hydroxide absorbs carbon dioxide and becomes the carbonate, which is insoluble. Salts of radium color the flame carmine.

Certain physiological effects of radium compounds are of interest. By exposure to radium rays the skin is burned, bacteria are destroyed or hindered in development, plants lose their chlorophyll, and seeds their power of germination.

Radium is a disintegration product of uranium, and is formed directly from ionium. It is found in all uranium minerals, and in the older minerals the amount present is directly proportional to the amount of uranium in the mineral, one part of radium being associated with approximately three million parts of uranium. Radium salts have been found to emit heat at a rate corresponding to about 132 gram calories per hour per gram of radium, and are thus able to maintain their temperature considerably above that of their surroundings.

Pure radium, free from its disintegration products, gives out only  $\alpha$  rays, but owing to the presence of these products, ordinary radium salts emit all three types of radiation. The rate of disintegration of radium corresponds to the transformation of about thirty-five one-hundred-thousandths of its mass per year, and the time required for exactly half of any given quantity to completely disintegrate into other elements is about 2000 years. One of the non-radioactive products of the disintegration of radium is the rare gas helium, which is formed from the expelled  $\alpha$  particles, and there are many reasons for supposing that the final, stable form of matter ultimately attained after the series of radioactive changes is ordinary lead.

**Radium Products.** Seven successive radioactive disintegration products of radium have been identified. The first product formed is a gaseous element known as the *emanation*, which is incapable of entering into chemical combination, and in this respect is similar to argon and helium. It disintegrates rather rapidly, forming solid, active products which are deposited on the walls of a vessel containing the emanation, or on the surface of any object

with which it is in contact, in this manner giving rise to the phenomenon known as "induced" or "excited" activity. The emanation is condensed at the temperature of liquid air and converted into a gas again on warming. The emanation has been found to give a characteristic bright line spectrum, and its density has been shown to correspond to an atomic weight not very different from that of radium.

The products of radium emanation, taken in their order of production, are known as radium A, B, C, D, E and F. Radium D is commonly called "radio-lead," from the fact that it is separated with the lead from uranium minerals and shows a close similarity to lead in its chemical behavior. Radium F is better known as polonium. It was the first of the strongly radioactive substances to be identified, and was discovered in 1898 by P. and S. Curie. It emits only  $\alpha$  rays and is half transformed in a period of 136 days. It has not been obtained pure in sufficient quantity to make a determination of its spectrum or atomic weight possible. It is separated with the bismuth from uranium minerals and exhibits a chemical behavior similar to that of both bismuth and tellurium.

### ACTINIUM, Ac.

The radio-element known as actinium was separated from uranium minerals by Debierne in 1899. It has not yet been possible to determine either its spectrum or its atomic weight. Its rate of transformation is also unknown, but it is probably very slow, since actinium preparations retain their activity unimpaired for considerable periods. Actinium is apparently a disintegration product of uranium and occurs in exceedingly small proportions in all uranium minerals. It is separated with the rare earths and is finally obtained associated with the lanthanum.

**Actinium Products.** Seven successive radioactive products of the disintegration of actinium have been identified.

These taken in their order are radioactinium, actinium X, actinium emanation, actinium A, B, C and D. But little is known concerning the chemistry of these products. Actinium emanation is a gas, apparently inert like the radium emanation, and similarly condensed at the temperature of liquid air.

### THORIUM, Th, 232.4.

The radioactivity of thorium was independently discovered by C. G. Schmidt and Mme. Curie in 1898. The rate of transformation of thorium has not yet been definitely determined, but is undoubtedly slower even than that of uranium. According to Hahn the disintegration of thorium is accompanied by the expulsion of  $\alpha$  particles, but ordinary thorium salts containing disintegration products of thorium emit all three types of radiation.

**Thorium Products.** Eight successive radioactive disintegration products of thorium have been identified. These, taken in the order of their production, are known as mesothorium 1, mesothorium 2, radiothorium, thorium X, emanation, thorium A, thorium B, thorium C, thorium C<sub>2</sub> and thorium D. Mesothorium 1 and thorium X appear to have chemical properties similar to barium, while radiothorium resembles thorium so closely in its chemical behavior that a direct, chemical separation of these two elements has not yet been effected. The thorium emanation, like the other emanations, exhibits the characteristics of an inert gas of the argon family, and is condensed at the temperature of liquid air. Very little is known concerning the chemical properties of the other members of this series.

References: Radio-Activity, by E. Rutherford (second edition), Cambridge University Press, 1905; Radioactive Transformations, by E. Rutherford, Charles Scribner's Sons, New York, 1906; Die Radioaktivität, by W. Marckwald, Ber. d. chem. Ges., XLI, 1524, 1908.



TABLE OF RADIOACTIVE ELEMENTS.

SHOWING THE TYPE OF RADIATION EMITTED BY EACH ELEMENT, ITS CONSTANT OF CHANGE, AND THE TIME REQUIRED FOR ONE-HALF OF ANY GIVEN QUANTITY TO DISINTEGRATE INTO OTHER FORMS OF MATTER. (According to Rutherford.)

Name.	Radiation emitted.	Disintegration Constant.	Half-value Period.
Uranium .....	$\alpha$	$1.16 \times 10^{-10} \text{ (year)}^{-1}$	$6 \times 10^8 \text{ years.}$
Uranium X .....	$\beta, \gamma$	$3.15 \times 10^{-2} \text{ (day)}^{-1}$	22 days.
Ionium .....	$\alpha$	?	?
Radium .....	$\alpha$	$3.5 \times 10^{-4} \text{ (year)}^{-1}$	2000 years.
Radium emanation .....	$\alpha$	$1.8 \times 10^{-1} \text{ (day)}^{-1}$	3.8 days.
Radium A .....	$\alpha$	$3.85 \times 10^{-3} \text{ (sec.)}^{-1}$	3 minutes.
Radium B .....	$\beta$	$4.4 \times 10^{-4} \text{ (sec.)}^{-1}$	26 minutes.
Radium C .....	$\alpha, \beta, \gamma$	$6.1 \times 10^{-4} \text{ (sec.)}^{-1}$	19 minutes.
Radium D .....	$\beta$	$4.2 \times 10^{-3} \text{ (year)}^{-1}$	16.5 years.
Radium E .....	$\beta$	$1.44 \times 10^{-1} \text{ (day)}^{-1}$	4.8 days.
Radium F } Polonium }	$\alpha$	$5.1 \times 10^{-3} \text{ (day)}^{-1}$	136 days.
Actinium .....	no rays	?	?
Radioactinium .....	$\alpha$	$3.5 \times 10^{-2} \text{ (day)}^{-1}$	19.5 days.
Actinium X .....	$\alpha$	$6.8 \times 10^{-2} \text{ (day)}^{-1}$	10.2 days.
Actinium emanation .....	$\alpha$	$1.8 \times 10^{-1} \text{ (sec.)}^{-1}$	3.9 seconds.
Actinium A .....	no rays	$3.2 \times 10^{-4} \text{ (sec.)}^{-1}$	36 minutes.
Actinium B .....	$\alpha, \beta, \gamma$	$5.4 \times 10^{-3} \text{ (sec.)}^{-1}$	2.1 minutes.
Thorium .....	$\alpha$	?	?
Mesothorium 1 .....	no rays	$1.2 \times 10^{-1} \text{ (year)}^{-1}$	5.5 years.
Mesothorium 2 .....	$\beta$	$3.1 \times 10^{-5} \text{ (sec.)}^{-1}$	6.2 hours.
Radiothorium .....	$\alpha$	$9.4 \times 10^{-4} \text{ (day)}^{-1}$	737 days.
Thorium X .....	$\alpha$	$2.2 \times 10^{-6} \text{ (sec.)}^{-1}$	3.6 days.
Thorium emanation .....	$\alpha$	$1.3 \times 10^{-4} \text{ (sec.)}^{-1}$	54 seconds.
Thorium A .....	$\beta$	$1.8 \times 10^{-5} \text{ (sec.)}^{-1}$	10.6 hours.
Thorium B .....	$\alpha$	$2.2 \times 10^{-4} \text{ (sec.)}^{-1}$	55 minutes.
Thorium C .....	$\alpha, \beta, \gamma$	?	a few seconds.

## CHAPTER IV.

### THE RARE EARTHS.\*

The rare earth elements may conveniently be classified as follows:

- I. THE YTTRIUM GROUP, consisting of
  1. Yttrium.
  2. Erbium.
  3. Holmium.
  4. Thulium.
  5. Dysprosium.
  6. Ytterbium.  
(Neoytterbium.)
  - (Lutecium.)
  7. Victorium.†
- II. THE TERBIUM GROUP, consisting of
  1. Terbium.‡
  2. Gadolinium§.
- III. THE CERIUM GROUP, consisting of
  1. Cerium.
  2. Lanthanum.
  3. Neodymium.
  4. Praseodymium.
  5. Samarium.
  6. Scandium.
  7. Decipium.†
  8. Europium.
- IV. THORIUM.
- V. ZIRCONIUM.

The rare earths occur so closely associated that it will be advantageous to consider their occurrence and their separation before taking them up separately.

**Occurrence.**||—Mineral sources of the rare earths are as follows:

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\* The term *earth* is applied to certain metallic oxides which were formerly regarded as elementary bodies, as  $Y_2O_3$ ,  $Er_2O_3$ ,  $La_2O_3$ , etc., and names ending in *a* are often used in designating them, as yttria, erbia, etc. The ending *um* designates the element, as yttrium, erbium, lanthanum.

† Classification still doubtful.

‡ Placed by some in yttrium group.

§ Placed by some in cerium group.

|| See also Schilling, *Das Vorkommen der seltenen Erden*, R. Oldenbourg, München, 1904.

## MINERAL SOURCES OF THE RARE EARTHS.

		Per cent Y Earths, Y <sub>2</sub> O <sub>3</sub> , etc.	Per cent Ce Earths, Ce <sub>2</sub> O <sub>3</sub> , etc.	Per cent ThO <sub>2</sub> .	Per cent ZrO <sub>2</sub> .
Adelfolite, <i>vid.</i> Zircon . . . . .	..... II III HR R <sub>2</sub> Si <sub>2</sub> O <sub>13</sub>	o-trace	o-trace	o-trace	53-66
Allanite . . . . .	.....	0-4	2-34	0-3	.....
Alvite, <i>vid.</i> Zircon . . . . .	.....	0-22	0-3	0-15	4-32
Anderbergite, <i>vid.</i> Zircon . . . . .	.....	7-10	0-0.2	0-1	41-60
Artfresonite . . . . .	Complex silicate	.....	.....	.....	1-7
Astrophyllite . . . . .	Complex silicate	.....	.....	.....	1-5
Auerbachite, <i>vid.</i> Zircon . . . . .	.....	.....	.....	.....	38-69
Auerue, * <i>vid.</i> Thorite . . . . .	.....	.....	.....	.....	69-72
Azorite, <i>vid.</i> Zircon . . . . .	.....	.....	.....	.....	66-67
Bagrationite, <i>vid.</i> Allanite . . . . .	.....	.....	.....	.....	.....
Beccarite, <i>vid.</i> Zircon . . . . .	.....	3-4	.....	.....	.....
Beckelith . . . . .	.....	.....	.....	.....	62-63
Bodenite, <i>vid.</i> Allanite . . . . .	.....	2-3	59-66	.....	2-3
Britholite, <i>vid.</i> Carpalenite . . . . .	Ca <sub>2</sub> (Y,Ce,La,Di) <sub>4</sub> (Si,Zr) <sub>2</sub> O <sub>15</sub>	17-18	circa 18	.....	.....
Bucklandite, <i>vid.</i> Allanite . . . . .	.....	.....	60-61	.....	.....
Calciotothorite, <i>vid.</i> Thorite . . . . .	.....	.....	circa 1	.....	.....
Capelenite . . . . .	.....	.....	.....	.....	.....
Caryocerite . . . . .	Complex silicate	52-53	3-"	.....	.....
<i>Catapleite</i> . . . . .	Complex silicate	2-3	34-36	13-14	.....
.....	H <sub>4</sub> (Na <sub>2</sub> ,Ca)ZrSi <sub>2</sub> O <sub>11</sub>	.....	.....	.....	29-40
.....	H <sub>4</sub> Ca <sub>2</sub> (Y,Er) <sub>2</sub> CSi <sub>4</sub> O <sub>17</sub>	37-38	.....	.....	.....
Cenosite . . . . .	.....	.....	.....	.....	.....
Cerite, <i>vid.</i> Cerite . . . . .	.....	.....	.....	.....	.....
Cerine, <i>vid.</i> Allanite . . . . .	.....	.....	.....	.....	.....
Cerinstein, <i>vid.</i> Cerite . . . . .	.....	.....	24-27	.....	.....
<i>Cerite</i> * . . . . .	.....	.....	.....	.....	.....
Certitanite <sub>2</sub> , <i>vid.</i> Cerite . . . . .	(Ca,Fe)(CeO)(Ce <sub>2</sub> 3OH)(SiO <sub>2</sub> ) <sub>2</sub>	0-7	36-72	0-0.7	0-11
Clintonite, . . . . .	.....	.....	.....	.....	0.7-2
Cytrolite, <i>vid.</i> Zircon . . . . .	Complex silicate	.....	.....	.....	41-42
.....	.....	8-14	0-3	0-1	.....

\* See note, page 42.

## MINERAL SOURCES OF THE RARE EARTHS—Continued.

		Per cent Y Earths, Y <sub>2</sub> O <sub>3</sub> , etc.	Per cent Ce Earths, Ce <sub>2</sub> O <sub>3</sub> , etc.	Per cent ThO <sub>2</sub> .	Per cent ZrO <sub>2</sub> .
Deweylite .....	4MgO, 3SiO <sub>2</sub> , 6H <sub>2</sub> O	.....	3-4	.....	.....
Elpidite .....	H <sub>2</sub> Na <sub>2</sub> ZrSi <sub>4</sub> O <sub>12</sub>	.....	.....	.....	20-21
Emerylite .....	Complex silicate	.....	.....	.....	circa 4
Epidote .....	Complex silicate	circa 1.5	circa 1	.....	.....
Erdmannite .....	Complex silicate	0-2	17-35	0-10	0-5
Eucolite, <i>vid.</i> Thorite .....	.....	circa 6	circa 14	circa 36	12-16
Eudialyte .....	.....	0-0.3	0-5	.....	circa 0.6
Eucrasite, <i>vid.</i> Thorite .....	Na <sub>13</sub> (Ca, Fe) <sub>6</sub> Cl(Si, Zr) <sub>10</sub> O <sub>42</sub>	.....	31-32	28-29	11-17
Freivalite, <i>vid.</i> Thorite .....	FeBe <sub>2</sub> Y <sub>2</sub> Si <sub>2</sub> O <sub>10</sub>	22-46	0-51	0-0.9	circa 6
Gadolinite .....	.....	.....	.....	.....	.....
Gymnite, <i>vid.</i> Deweylite .....	.....	.....	.....	.....	.....
Hainite, <i>vid.</i> Låvenite .....	4Ca(Si, Zr) <sub>3</sub> O <sub>3</sub> ·Na <sub>2</sub> ZrO <sub>3</sub> F <sub>3</sub>	.....	.....	.....	21-22
Hortdahlite .....	Complex silicate	.....	circa 2	.....	.....
Hyacinth, <i>vid.</i> Zircon .....	.....	.....	.....	.....	.....
Hypoclerite .....	Complex silico-titanate	1-2	12-13	0-0.8	.....
Jargon, <i>vid.</i> Zircon .....	Complex silicate	6-9	0-0.6	.....	.....
Johnstrupite .....	R(Si, Zr) <sub>3</sub> O <sub>3</sub> ·Zr(SiO <sub>3</sub> ) <sub>2</sub> ·RTa <sub>2</sub> O <sub>6</sub>	.....	.....	.....	28-32
Keilhauite* .....	.....	.....	.....	.....	.....
Låvenite .....	.....	.....	.....	.....	.....
Mackintoshite .....	UO <sub>2</sub> ·3ThO <sub>2</sub> ·3SiO <sub>2</sub> ·3H <sub>2</sub> O	.....	1-2	circa 45	circa 1
Malakon, <i>vid.</i> Zircon .....	.....	.....	.....	.....	.....
Manganepidote, <i>vid.</i> Epidote .....	Complex silicate	9-10	circa 45	1-2	circa 0.5
Melanocerite .....	.....	.....	.....	.....	.....
Mosandrite* <i>vid.</i> Gadolinite .....	Complex silico-titanate	0-3	16-26	.....	.....
Mosandrite .....	.....	37-38	8-10	.....	2-3
Murmontite, <i>vid.</i> Allanite .....	.....	.....	.....	.....	.....
Ochroite, <i>vid.</i> Cerite .....	.....	.....	.....	.....	.....

\* See note, page 42.

## MINERAL SOURCES OF THE RARE EARTHS—Continued.

		Per cent Y Earths, Y <sub>2</sub> O <sub>3</sub> , etc.	Per cent Ce Earths, Ce <sub>2</sub> O <sub>3</sub> , etc.	Per cent ThO <sub>2</sub>	Per cent ZrO <sub>2</sub>
Orthite, * <i>vid.</i> Allanite.	.....	.....	.....	.....	.....
Ostranite, <i>vid.</i> Zircon	.....	.....	.....	.....	.....
Piedmontite	.....	1-2	circa 1	.....	.....
Pyrothite, <i>vid.</i> Allanite	.....	.....	.....	.....	.....
Retzian	.....	circa 10	.....	.....	.....
Riebeckite, <i>vid.</i> Arfvedsonite	.....	.....	.....	.....	0.7-7
Rinkite	.....	.....	.....	.....	.....
Rosenbuschite	.....	0-1	13-26	.....	.....
Rowlandite	.....	.....	0.3-2.4	.....	18-20
Schelite, <i>vid.</i> Epidote	.....	61-62	.....	.....	.....
Serpentine	.....	.....	.....	.....	.....
Sillimanite	.....	.....	1-2	.....	.....
Steenstrupine, <i>vid.</i> Caryocerite	.....	.....	.....	.....	0-18 ?
Tachyphalinite, <i>vid.</i> Zircon	.....	0-16	14-35	2-7	.....
Tautolite, <i>vid.</i> Allanite	.....	.....	.....	.....	.....
Thalénite	.....	58-63	.....	.....	.....
<i>Thorite</i>	.....	{ 0-7			o-traces
<i>Thorogummite</i>	.....	.....	.....	48-72	.....
Thortveitite	.....	circa 40%	.....	41-43	.....
	.....	Sc <sub>2</sub> O <sub>3</sub>	circa 26	.....	.....
Thulite	.....	.....	.....	.....	.....
Tritomite	.....	0-4-3	44-59	0-9	0-4
Tscheffkinit	.....	0-3	23-47	0-21	0-2
Uralorthite, <i>vid.</i> Allanite	.....	.....	.....	.....	.....
Wasite, <i>vid.</i> Allanite	.....	.....	.....	.....	.....
<i>Wöhlerite</i>	.....	.....	0-0.6	.....	15-23
Xanthorthite, <i>vid.</i> Allanite	.....	.....	.....	.....	.....
Ytterbite, <i>vid.</i> Gadolinite	.....	.....	.....	.....	.....

\* See note, page 42.

## MINERAL SOURCES OF THE RARE EARTHS—Continued.

		Per cent Y Y <sub>2</sub> O <sub>3</sub> , etc.	Per cent Ce Ce <sub>2</sub> O <sub>3</sub> , etc.	Per cent ThO <sub>2</sub>	Per cent ZrO <sub>2</sub>
Yttrilite .....	<sup>III</sup> R <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>	46-47	5-8	10-12	.....
Ytrotitanite, <i>vid.</i> Keilhauite .....	.....	5-10	0.3-0.5	.....	.....
Zircon .....	ZrSiO <sub>4</sub>	0-3	.....	0-2	61-70
Zirconite, <i>vid.</i> Zircon .....	.....	.....	.....	.....	.....
<i>Äschynite</i> .....	<sup>III</sup> R <sub>2</sub> Nb <sub>4</sub> O <sub>18</sub> ·R <sub>3</sub> (Ti, Th) <sub>6</sub> O <sub>18</sub>	1-3	15-23	13-23	0-20
Alshedite, <i>vid.</i> Titanite .....	.....	2-3	.....	.....	.....
Ännerrödite .....	Complex	7-8	2-3	2-3	1-2
Blomstrandine-Priorite .....	Complex	17-29	1-4	1-8	0-1
Bragite, <i>vid.</i> Fergusonite .....	.....	33-37	3-7	.....	0-1
Chalcolamprite, <i>vid.</i> Pyrochlore .....	.....	.....	3-4	.....	5-6
Columbite .....	(Fe, Mn)(Nb, Ta) <sub>2</sub> O <sub>6</sub>	1-4	0-0.5	.....	0-0.7
Delorenzite .....	2FeO·UO <sub>2</sub> ·2Y <sub>2</sub> O <sub>3</sub> ·24TiO <sub>2</sub> ?	14-15	.....	.....	.....
Dysanelyte .....	Complex titanio-niobate	0-5	0.1-6	.....	.....
Endeolite, <i>vid.</i> Pyrochlore .....	.....	.....	4-5	.....	.....
Eucolite-titanite, <i>vid.</i> Titanite .....	.....	circa 0.6	2-3	circa 0.2	3-4
<i>Euzeinite</i> .....	<sup>III</sup> R(NbO <sub>3</sub> ) <sub>8</sub> ·R <sub>2</sub> (TiO <sub>2</sub> ) <sub>3</sub> H <sub>2</sub> O	13-30	2-8	0-6	0-2
<i>Fergusonite</i> .....	<sup>III</sup> R(Nb, Ta) <sub>2</sub> O <sub>4</sub>	30-46	0-9	0-3	0-7
Fluochlore, <i>vid.</i> Pyrochlore .....	.....	0.7-0.9	5-15	.....	0-5
Guarinite .....	CaTiSiO <sub>3</sub>	circa 1	3-4	.....	.....
Hatchettolite .....	R(Nb, Ta) <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	.....	0-2	.....	.....
Hielmite .....	Complex	1-5	0.4-1	.....	.....
Knopite, <i>vid.</i> Perovskite .....	.....	.....	4-7	.....	0-1
Kochelite, <i>vid.</i> Fergusonite .....	.....	17-18	.....	1-2	12-13
Koppite, <i>vid.</i> Pyrochlore .....	.....	.....	4-11	.....	0-5

## MINERAL SOURCES OF THE RARE EARTHS—Continued.

		Per cent Y Earths, Y <sub>2</sub> O <sub>3</sub> , etc.	Per cent Ce Earths, Ce <sub>2</sub> O <sub>3</sub> , etc.	Per cent ThO <sub>2</sub> .	Per cent ZrO <sub>2</sub> .
Leukosphenite .....	Complex silico-titanate	.....	.....	.....	3-4
Loranskite, <i>vid.</i> Euxenite .....	.....	10	3	20	.....
Madupite .....	Silico-titano-carbonate	.....	0.1	.....	.....
Margnacite, <i>vid.</i> Pyrochlore .....	.....	circa 5	13-14	0.2	.....
Microlite .....	Ca <sub>2</sub> Ta <sub>2</sub> O <sub>7</sub>	0-7	0-4	.....	.....
Nephelesyenite .....	Complex silico-titanate	.....	.....	.....	circa 1
Niobite, <i>vid.</i> Columbite .....	.....	.....	.....	.....	0.1-0.5
Nohelite, <i>vid.</i> Samarskite .....	.....	14-15	0.25	.....	2-3
Oerstedite, <i>vid.</i> Zircon .....	Complex silico-titano-carbonate	.....	.....	.....	.....
Orendite .....	CaTiO <sub>3</sub>	5-6	0.1	.....	0.22
Perovskite .....	.....	.....	.....	.....	.....
<i>Polycrase</i> .....	$\text{R}^{\text{III}}(\text{NbO}_2)_2 \cdot 2\text{R}^{\text{III}}(\text{TiO}_2)_2 \cdot 3\text{H}_2\text{O}$	20-32	0-3	0-3.5	.....
<i>Polymignite</i> .....	$5\text{RTiO}_2 \cdot 5\text{RZrO}_2 \cdot \text{R}(\text{Nb}, \text{Ta})_2\text{O}_6$	2-3	2-11	3-4	29-30
Pyrochlore* .....	$\text{RNb}_2\text{O}_6 \cdot \text{R}(\text{Ti}, \text{Th})\text{O}_2$	.....	5-10	0-8	.....
Rogersite .....	Complex	60-61	.....	.....	.....
<i>Samarskite</i> .....	$\text{R}^{\text{III}}\text{R}_2(\text{Nb}, \text{Ta})_4\text{O}_{22}$	5-21	2-5	0-6	0-4
Spyrlite .....	Complex	27-28	9-10	.....	circa 2
Tantalite .....	$\text{FeTa}_2\text{O}_6$	.....	.....	.....	1-11
Tapiolite, <i>vid.</i> Tantalite .....	.....	.....	.....	.....	.....
Titanite .....	.....	.....	0.5-2	.....	.....
Tyrite, <i>vid.</i> Fergusonite .....	$\text{CaTiSiO}_6$	28-36	4-9	.....	0-3
Vietinghofite, <i>vid.</i> Samarskite .....	.....	6-7	1-2	.....	circa 1
Wilkie† .....	.....	7-8	2-3	5-6	+TiO <sub>2</sub>
Ytterrolmenite, <i>vid.</i> Samarskite .....	.....	.....	.....	.....	23-24
Yttrocasite .....	Complex titanate	25-26	2-3	8-9	.....

\* Contains more than 1% of Sc<sub>2</sub>O<sub>3</sub>. See note, page 42.

† See note, page 42.

## MINERAL SOURCES OF THE RARE EARTHS—Continued.

		Per cent Y Earths, Y <sub>2</sub> O <sub>3</sub> , etc.	Per cent Ce Earths, Ce <sub>2</sub> O <sub>3</sub> , etc.	Per cent ThO <sub>2</sub>	Per cent ZrO <sub>2</sub>
<i>Ytrotantalite</i> . . . . .	$\text{H}^{\text{III}} \text{RR}_2(\text{Ta}, \text{Nb})_2\text{O}_{18} \cdot 4\text{H}_2\text{O}$	17-38	0-2	.....	.....
<i>Ytrotitanite, vid. Keilhauite</i> . . . . .	$(\text{Ca}, \text{Fe})\text{O} \cdot 2(\text{Zr}, \text{Ti}, \text{Th})\text{O}_2$	0-2	2-3	.....	.....
<i>Zirkelite</i> . . . . .	$\text{Ca}_2\text{P}_2\text{O}_7(\text{Ca}(\text{F}(\text{Cl})))$	.....	0-5	.....	50-53
<i>Apatite</i> . . . . .	$\text{H}^{\text{II}} \text{R}_2(\text{PO}_4)_3 \cdot 4\text{H}_2\text{O}$	.....	.....	.....	.....
<i>Castelnaudite, vid. Xenotime</i> . . . . .	.....	.....	50-51	.....	.....
<i>Churchite</i> . . . . .	.....	.....	.....	.....	.....
<i>Cryptolite, vid. Monazite</i> . . . . .	.....	.....	.....	.....	.....
<i>Edwardsite, vid. Monazite</i> . . . . .	.....	.....	.....	.....	.....
<i>Eremite, vid. Monazite</i> . . . . .	.....	.....	28	.....	.....
<i>Florentite</i> . . . . .	Complex phospho-silicate	.....	.....	.....	.....
<i>Hussakite, vid. Xenotime</i> . . . . .	.....	.....	.....	.....	.....
<i>Mengite, vid. Monazite</i> . . . . .	$(\text{Ce}, \text{La}, \text{Di})\text{PO}_4$	0-5	39-74	0-18	0-7
<i>Monazite</i> . . . . .	$\text{RPO}_4 \cdot \text{H}_2\text{O}$	2-10	53-58	.....	.....
<i>Monazitoid, vid. Monazite</i> . . . . .	.....	.....	.....	.....	.....
<i>Rhabdophanite</i> . . . . .	$\text{YPO}_4$	54-64	0-11	0-3	0-2
<i>Scovillite, vid. Rhabdophanite</i> . . . . .	.....	.....	.....	.....	.....
<i>Turnerite, vid. Monazite</i> . . . . .	.....	.....	.....	.....	.....
<i>Xenotime</i> . . . . .	.....	.....	.....	.....	.....
<i>Ancylite</i> . . . . .	$4\text{Ce}(\text{OH})\text{CO}_3 \cdot 3\text{SrCO}_3 \cdot 3\text{H}_2\text{O}$	.....	46-47	0-2	.....
<i>Bastnäsile</i> . . . . .	$(\text{Ce}, \text{La}, \text{Di})_2(\text{CO}_3)_3(\text{Ce}, \text{La}, \text{Di})\text{F}_3$	.....	64-93	0-10	.....
<i>Cordylite, vid. Parisite</i> . . . . .	.....	.....	49-50	0-3	.....
<i>Hamartite, vid. Bastnäsile</i> . . . . .	.....	.....	.....	.....	.....
<i>Hydrocerite, vid. Lanthanite</i> . . . . .	.....	.....	.....	.....	.....
<i>Lanthanite</i> . . . . .	$\text{La}_2(\text{CO}_3)_3 \cdot 9\text{H}_2\text{O}$	.....	55La <sub>2</sub> O <sub>3</sub>	.....	.....



## MINERAL SOURCES OF THE RARE EARTHS—Continued.

		Per cent Y, Er, Th, Y <sub>2</sub> O <sub>3</sub> , etc.	Per cent Ce, Pr, La, CeO <sub>2</sub> , etc.	Per cent ThO <sub>2</sub>	Per cent ZrO <sub>2</sub>
Musite, <i>vid.</i> Parisite	.....	.....	.....	.....	.....
Parisite	.....	0-2.5	51-64	.....	.....
Synchisite	.....	1-2	50-51	0-0.3	.....
Tengerite	.....	40-41	circa 7	.....	.....
Weibyeite, <i>vid.</i> Parisite	.....	.....	66-67	.....	.....
Fluocerite	.....	1-4	81-83	.....	.....
Hydrofluocerite, <i>vid.</i> Fluocerite	.....	.....	.....	.....	.....
Tysonite	.....	.....	69-70	.....	.....
Ytrocercite	.....	8-15	9-16	.....	.....
Danburite	.....	0.85	.....	.....	.....
Homilite	.....	.....	0.2-2.5	.....	.....
Nordenskiöldine	.....	.....	.....	.....	0.9
Baddeleyite	.....	.....	.....	.....	96-97
Brazilite, <i>vid.</i> Baddeleyite	.....	.....	.....	.....	.....
Thorianite, <i>vid.</i> Uraninite	.....	.....	1-8	70-80	0-3.5
Pyrolusite	.....	0.1	.....	.....	.....
Nivenite, <i>vid.</i> Uraninite	.....	11-12	.....	7-8	.....
Uraninite	.....	0-10	0-3	1-11	0-8
Uranothorite, <i>vid.</i> Thorite	.....	.....	.....	.....	.....
Uranophane, <i>vid.</i> Uraninite	.....	.....	.....	.....	.....
Uranotil, <i>vid.</i> Uraninite	.....	.....	.....	.....	.....
Ytrogummite, <i>vid.</i> Uraninite	.....	.....	.....	.....	.....

\* Crookes (Proc. Royal Soc. (London) Lxxx (A), 516), has shown scandium to be widely distributed. The minerals starred contain over 0.01%. Eberhard, in examination of over 350 minerals and rocks, found the spectrum of scandium (group of lines between 3535.86 and 3651.98, with brightest at 3613.98) rarely absent. He mentions wolframite, cassiterite and monazite especially. (Sitzungber. Akad. Sci. Berlin, 1908, 851; and 1910, 404.)

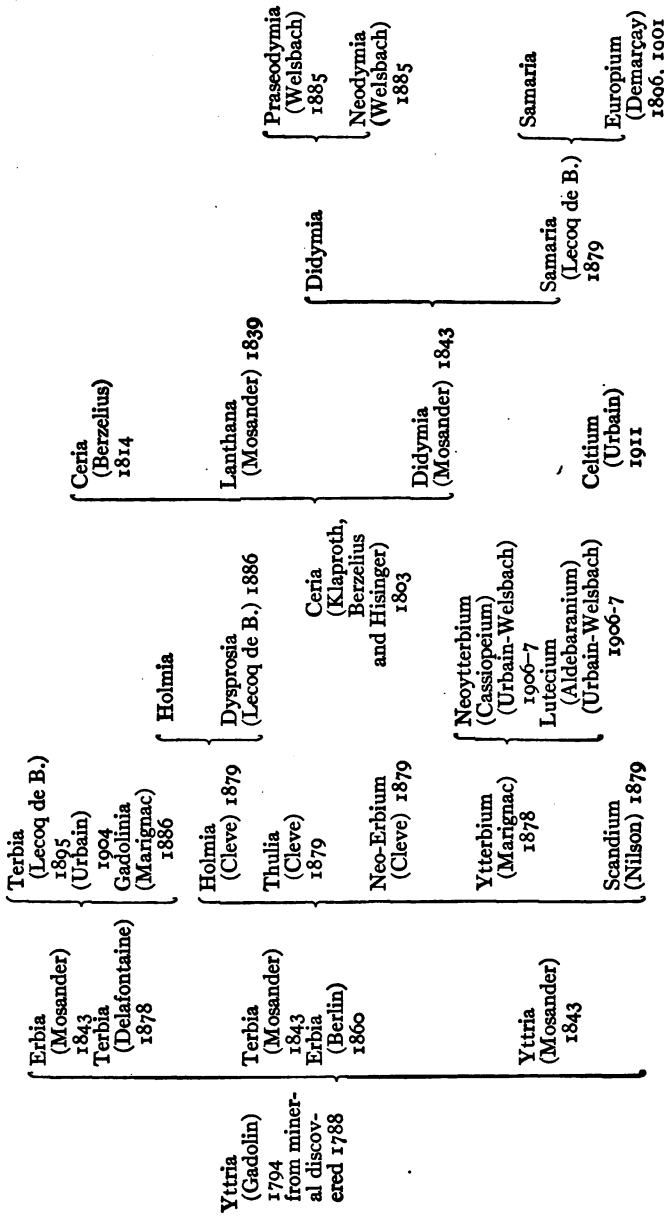
**Separation.** The methods of separation here enumerated without reference to original sources are described in full in Böhm's "*Darstellung der seltenen Erden*," volume 1, pages 108 to 490.

- (1) Ignition of the nitrates, carbonates, or oxalates, and treatment of the product with ammonium nitrate, ammonium chloride, or dilute acid.
- (2) Treatment of suspended hydroxides with chlorine.
- (3) Oxidation with potassium permanganate.
- (4) Treatment with peroxides, as  $\text{PbO}_2$ , etc.
- (5) Oxidation with hydrogen dioxide or sodium dioxide.
- (6) Treatment with persulphates.
- (7) Treatment with the electric current.
- (8) Formation of basic nitrates.
  - (a) By treating the nitrates with oxides.
  - (b) By treating the neutral nitrates with hot water.
- (9) Formation of basic chlorides.
  - (a) By treating the chlorides with water.
  - (b) By treating the chlorides with magnesium oxide or copper oxide.
- (10) Formation of basic sulphates by the action of water.
- (11) Fractional precipitation with ammonium hydroxide.
- (12) Fractional precipitation with sodium or potassium hydroxide.
- (13) Partial precipitation with anilin.
- (14) Precipitation by alkali hyponitrides.
- (15) Precipitation by sulphurous acid and sulphites.
- (16) Precipitation by sodium thiosulphate.
- (17) Precipitation by carbonates.
- (18) Precipitation as chromates.
- (19) Precipitation by formates.
- (20) Precipitation by acetates.
- (21) Action of dilute acid upon the oxalates.
- (22) Precipitation as the sulphates.
- (23) Fractional crystallization of the nitrates.

- (24) Action of alcohol upon the nitrates.
- (25) Action of (a) acetylacetone, (b) ethylsulphate, (c) salts of sulphanilic acid.
- (26) Fractional crystallization of the double salts:
  - (a) Double sulphates with alkali sulphates.
  - (b) Double nitrates with ammonium nitrate.
  - (c) Double nitrates with magnesium nitrate.
  - (d) Double nitrates with bismuth nitrate.
  - (e) Double fluorides with alkali and magnesium fluorides.
- (27) Action of (a) neutral or acid potassium oxalate; (b) ammonium oxalate.
- (28) Fractional crystallization of the bromates (James, Jour. Amer. Chem. Soc. xxx, 182).
- (29) Fractional precipitation of the succinates (Lenher, Jour. Amer. Chem. Soc. xxx, 572).
- (30) Action of ammonium carbonate upon the oxalates (James, Jour. Amer. Chem. Soc. xxix, 495).
- (31) Fractional precipitation by potassium stearate (Stoddart and Hill, Jour. Amer. Chem. Soc. xxxiii, 1076).
- (32) Fractional crystallization of the picrates (Dennis and Bennett, Jour. Amer. Chem. Soc. xxxiv, 7).

The separation of the rare earths cannot be made with quantitative accuracy. For working schemes, however, the student is referred to methods worked out by James (Jour. Amer. Chem. Soc. xxx, 979; and xxxiv, 757) and diagrammatically shown on pp. 213-15. These are the only schemes of separation that have come to the notice of the author, and they are followed in this book where methods are described at all in detail. It may be added that Urbain (Jour. chim. phys. iv, 31) has arranged the rare earths according to their solubilities as follows: lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium.

(Adapted with modifications and additions from Abegg's Handbuch der Anorganischen Chemie and Roscoe's Treatise on Chemistry.)



## I. THE YTTRIUM GROUP.

### 1. YTTRIUM, Y, 89.

**Discovery.** In the year 1794, Gadolin (Kongl. Vet. Acad. Handl. xv, 137; Crell Annal. (1796) 1, 313) discovered a new earth in a mineral later called Gadolinite, which had been discovered by Arrhenius and described by Geyer in 1788 (Crell Annal. (1788) 1, 229). In 1797 Ekeberg confirmed Gadolin's discovery and named the new earth Yttria (Kong. Vet. Acad. Handl. xviii, 156; Crell Annal. (1799) II, 63), deriving the name from Ytterby, the source of the mineral.

**Occurrence.** Yttrium occurs always in combination. Its chief sources are the minerals gadolinite and xenotime, and monazite residues (*vid.* Occurrence of Rare Earths, page 35).

**Extraction.** The following are common methods for the extraction of yttrium salts from minerals:

(1) *From gadolinite (or any other silicate).* The finely powdered mineral is mixed with common sulphuric acid until the mass has the consistency of thick paste. It is then heated until dry and hard, pulverized, and extracted with cold water. From this extraction the oxalates are precipitated by the addition of oxalic acid; they are then washed, dried, and heated at 400° C. The oxides thus obtained are dissolved in sulphuric acid, and the solution is saturated with potassium or sodium sulphate. The double sulphates of the cerium group are precipitated, and the members of the yttrium group remain in solution.

(2) *From gadolinite.* The mineral is decomposed by aqua regia (*vid.* Experiment 1).

(3) *From samarskite.* The mineral is decomposed by hydrofluoric acid. The niobic and tantalic acids go into

solution, and the yttrium earths, together with uranium oxide, remain (Lawrence Smith, Amer. Chem. Jour. V, 44).

**The Element.** *A. Preparation.* Elementary yttrium may be obtained (1) by heating the chloride with potassium (Berzelius); (2) by subjecting the melted double chloride of sodium and yttrium to electrolysis (Cleve, Bull. Soc. Chim. d. Paris [2] XVIII, 193); (3) by heating the oxide with magnesium (Winkler, Ber. Dtsch. chem. Ges. XXIII, 787).

*B. Properties.* Yttrium is a grayish-black powder, which decomposes water only slightly at ordinary temperatures, but more rapidly on boiling, forming the oxide. Ignited on platinum in the air, it burns to the oxide with a brilliant light; in oxygen with a very intense glow. It is very soluble in dilute acids, including acetic, but is only slightly soluble in concentrated sulphuric acid. It decomposes potassium hydroxide at the boiling temperature.

**Compounds.** *A. Typical forms.* The following are typical compounds of yttrium:

Oxide,  $Y_2O_3$ .

Hydroxide,  $Y(OH)_3$ .

Carbonates,  $Y_2(CO_3)_3 + 3H_2O$ ;  $Y_2(CO_3)_3 \cdot Na_2CO_3 + 4H_2O$ ;  
 $Y_2(CO_3)_3 \cdot (NH_4)_2CO_3 + 2H_2O$ .

Chlorides,  $YCl_3$ ;  $YCl_3 + 6H_2O$ ;  $YCl_3 \cdot 3HgCl_2 + 9H_2O$ ;  
 $YCl_3 \cdot 2AuCl_3 + 16H_2O$ ;  $2YCl_3 \cdot 3PtCl_2 + 24H_2O$ .

Chlorate,  $Y(ClO_3)_3 + 8H_2O$ .

Perchlorate,  $Y(ClO_4)_3 + 8H_2O$ .

Bromides,  $YBr_3$ ;  $YBr_3 + 9H_2O$ .

Bromate,  $Y(BrO_3)_3 + 9H_2O$ .

Iodide,  $YI_3$ .

Iodate,  $Y(IO_3)_3 + 3H_2O$ .

Periodate,  $Y_2O_3 \cdot I_2O_7 + 8H_2O$ .

Fluoride,  $YF_3 + 0.5H_2O$ .

Nitrates,  $Y(NO_3)_3 + 6H_2O$ ;  $2Y_2O_3 \cdot 3N_2O_5 + 9H_2O$ .

Cyanides,  $YKFe(CN)_6 + 2H_2O$ ;  $Y(SCN)_3 + 6H_2O$ .

Sulphates,  $Y_2(SO_4)_3 + 8H_2O$ ;  $Y_2(SO_4)_3 \cdot 4K_2SO_4$ ;  
 $Y_2(SO_4)_3 \cdot Na_2SO_4 + 2H_2O$ .

Sulphite,  $Y_2(SO_3)_3 + 3H_2O$ .

Seleniates,  $Y_2(SeO_4)_3 + 8H_2O$ ;  $Y_2(SeO_4)_3 \cdot K_2SeO_4 + 6H_2O$ ;  
 $Y_2(SeO_4)_3 \cdot (NH_4)_2SeO_4 + 6H_2O$ .

Selenites,  $Y_2(SeO_3)_3 + 12H_2O$ ;  $Y_2O_3 \cdot 4SeO_2 + 4H_2O$ .

Sulphide,  $Y_2S_3$ .

Oxalate,  $Y_2(C_2O_4)_3 + 9H_2O$ .

Phosphates,  $YPO_4$ ;  $Y(PO_3)_3$ ;  $YHP_2O_7 + 3.5H_2O$ .

Chromate,  $Y_2(CrO_4)_3 \cdot K_2CrO_4 + xH_2O$ .

Tungstate,  $Y_2(WO_4)_3 + 6H_2O$ .

Carbide,  $YC_2$ .

Organic compounds, *vid.* Platt and James, Jour. Amer. Chem. Soc. xxxiii, 1330.

**B. Characteristics.** The compounds of yttrium have few characteristic reactions. They resemble quite closely the compounds of aluminum, but yttrium differs from aluminum in having a hydroxide insoluble in excess of sodium or potassium hydroxide and in forming no alums. The salts of yttrium give no absorption spectra. Yttrium sulphate differs from the sulphate of cerium in forming no insoluble double sulphate with potassium or sodium sulphate. Most of the rare earth compounds except the sulphate, nitrate and halogen salts are insoluble.

**Estimation.** Yttrium is generally weighed as the oxide,  $(Y_2O_3)$ , which has been obtained by the ignition of the hydroxide or the oxalate.

**Separation.** In the course of analysis the yttrium earths are precipitated with the aluminum group. They may be separated from aluminum by precipitation with oxalic acid or ammonium oxalate in faintly acid solution; in this reaction they resemble the other members of the rare-earth group (Ce, La, Pr, Nd, Th, Zr, etc.). They may

be separated from these by saturating a solution of the sulphates with potassium sulphate; the yttrium earths do not form a double sulphate insoluble in potassium sulphate as do the others.

For the separation of yttrium from the very rare members of its group Methods 8, 9(a), 11, 18, 21 and 28 (page 43) have been used. James recommends the fractional crystallization of the bromates (28), and finds the yttrium in the fraction between the holmium and the erbium. Taking the fractions free from holmium, he converts them into the neutral nitrates. These nitrates of yttrium and erbium are boiled with the addition of magnesium oxide until the liquid shows no absorption bands of erbium.

## EXPERIMENTAL WORK ON YTTRIUM.

*Experiment 1. Extraction of yttrium salts from gadolinite* ( $\text{Be}_2\text{FeY}_2\text{Si}_2\text{O}_{10}$ ). Warm 5 grm. of finely powdered mineral with aqua regia until it is completely decomposed. Evaporate on a water-bath and desiccate to remove the silica. Extract with hot water and a little hydrochloric acid, and add to the extract ammonium oxalate until precipitation ceases. Filter off the precipitate, which consists of the oxalates of the yttrium and cerium groups, together with traces of the oxalates of manganese and calcium; dry and ignite. Dissolve in a small amount of hydrochloric acid the oxides thus obtained, and saturate the solution with potassium sulphate; this precipitates the members of the cerium group as the double sulphates. Filter, and wash with a solution of potassium sulphate. From the filtrate precipitate the yttrium earths by an alkali hydroxide or oxalate. To remove the manganese and calcium, dissolve the precipitate in nitric acid, evaporate to dryness, and heat until the manganese salt is decomposed. Extract with water, filter off the oxide of man-



ganese, treat the filtrate with ammonium hydroxide, and stir thoroughly. The calcium hydroxide will be dissolved, and the yttrium earths precipitated.

*Experiment 2. Precipitation of yttrium hydroxide* ( $\text{Y}(\text{OH})_3$ ). (a) To a solution of an yttrium salt add ammonium hydroxide.

(b) Repeat the experiment, using sodium or potassium hydroxide.

Note the insolubility in excess in each case.

(c) Precipitate yttrium hydroxide by the action of ammonium sulphide.

*Experiment 3. Precipitation of yttrium carbonate* ( $\text{Y}_2(\text{CO}_3)_3$ ). (a) To a solution of an yttrium salt add ammonium carbonate.

(b) Repeat the experiment, using sodium or potassium carbonate.

Note the solubility in the cold upon the addition of an excess of the alkali carbonates, and the reprecipitation on boiling.

(c) Try the action of the common acids upon yttrium carbonate.

*Experiment 4. Precipitation of yttrium oxalate* ( $\text{Y}_2(\text{C}_2\text{O}_4)_3$ ). To a solution of an yttrium salt add a solution of either oxalic acid or an alkali oxalate.

*Experiment 5. Precipitation of yttrium phosphates* ( $\text{Y}_2(\text{HPO}_4)_3$ ;  $\text{YPO}_4$ ). To a solution of an yttrium salt add sodium phosphate in solution ( $\text{Na}_2\text{HPO}_4$ ). The precipitate is said to be of the acid form  $\text{Y}_2(\text{HPO}_4)_3$ . The neutral phosphate ( $\text{YPO}_4$ ) is formed by treating an yttrium salt in solution with an ammoniacal phosphate.

*Experiment 6. Precipitation of yttrium ferrocyanide* ( $\text{YKFe}(\text{CN})_6$ ). To a solution of an yttrium salt add potassium ferrocyanide.

*Experiment 7. Precipitation of yttrium chromate* ( $x\text{Y}_2(\text{CrO}_4)_3 \cdot y\text{Y}_2\text{O}_3$ ). To a solution of an yttrium salt add a solution of potassium chromate, and neutralize if necessary.

*Experiment 8. Precipitation of yttrium fluoride (YF<sub>3</sub>).*  
To a solution of an yttrium salt add potassium fluoride.

*Experiment 9. Negative tests of yttrium salts.* Note that hydrogen sulphide gives no precipitate with yttrium salts, and that saturation of a solution of an yttrium salt with potassium or sodium sulphate gives no insoluble double salt.

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|----------------------------------|------------------------------------|
| 2. <b>ERBIUM</b> , Er, 167.7     | 6. <b>YTTERBIUM</b> , Yb, 173      |
| 3. <b>HOLMIUM</b> , Ho, 162      | ( <b>NEOYTTERBIUM</b> , Ny, 172 ±) |
| 4. <b>THULIUM</b> ,* Tm, 168.5   | ( <b>LUTECIUM</b> , Lu, 174 ±)     |
| 5. <b>DYSPROSIUM</b> , Dy, 162.5 | 7. <b>EUROPIUM</b> ,† Eu,* 152     |
| 8. <b>VICTORIUM</b> ,‡ Vc, 117   |                                    |

**Discovery.** In 1843 Mosander (J. pr. Chem. xxx, 288) announced, as the result of his investigation of yttria, its separation into three earths, two white and one yellow. To the less basic of the white oxides he gave the name Terbium earth, to the more basic the original name Yttrium earth, and the yellow oxide he called Erbium earth.

In 1879 Cleve (Compt. rend. LXXXIX, 478), while working on erbium earth, discovered two elements, Holmium and Thulium, which he separated as the oxides.

Seven years later Lecoq de Boisbaudran (Compt. rend. CII, 1004), announced the isolation of a new earth from the oxide of holmium, namely, that of Dysprosium.

In 1878 Marignac (Compt. rend. LXXXVII, 578) found in gadolinite the oxide of a new element which he named Ytterbium.

In 1906 Auer von Welsbach (Monatshefte f. Chem. xxvii, 935) announced that he had decomposed ytterbium by the action of ammonium oxalate on the double ammonium oxalate, and in 1907 Urbain (Compt. rend. CXLV, 759;

\* For the most recent work upon this earth, *vid.* James, Jour. Amer. Chem. Soc. XXXIII, 1332, 1363.

† Placed by some in Cerium Group.

‡ Considered by Urbain (Jour. chim. phys. iv, 321) to be gadolinium.

Chem. News xcvi, 271) stated that by subjecting Marignac's ytterbium to fractional crystallization in nitric acid he had separated it into two elements, which he called Neoytterbium and Lutecium.

Four years later, while subjecting the gadolinite earths to fractional crystallization in nitric acid, Urbain obtained a mother liquor from which he separated an oxide of very low magnetic susceptibility. The arc spectrum showed many new lines, some very intense. The new earth proved to be in chemical character between lutecium and scandium. The name Celtium was proposed, and the symbol Ct (Compt. rend. clII, 141; Chem. Ztg. xxxv, 161).

Demarçay, in 1901 (Compt. rend. cxxxII, 1484), isolated a colorless earth closely associated with samarium, and named the new element Europium. This earth, the existence of which had for some years been recognized by himself and by others, had been designated by him as  $\Sigma$ , and by Lecoq de Boisbaudran as  $Z_{\epsilon}$ .

In 1899 Crookes (Chem. News LXXIX, 212) separated from the yttrium earths by fractional fusion of the nitrates and fractional crystallization of the oxalates a new substance having a group of lines in the ultra violet. This substance he at first called Monium and later Victorium (Proc. Royal Soc. LXV, 237).

**Occurrence.** These very rare earths are found in small quantities and varying proportions associated with yttria (*vid.* Occurrence of Rare Earths, page 35). Their chief sources are as follows: of erbium, gadolinite, yttrotantalite, euxenite, sipylite, xenotime; of ytterbium, gadolinite, sipylite, xenotime, euxenite; of holmium, thulium and dysprosium, gadolinite, keilhauite, euxenite, samarskite; of europium, samarskite, orthite, cerite, gadolinite, keilhauite; of victorium, crude yttrium earths.

**Extraction.** Methods for the extraction of the yttrium earths have been already given (*vid.* Extraction of Yttrium, page 46).

	Er	Yb
Oxides.....	$\text{Er}_2\text{O}_3$ $\text{Er}_2\text{O}_5$	$\text{Yb}_2\text{O}_3$
Hydroxides.....	$\text{Er}_2\text{O}(\text{OH})_4$	$\text{Yb}_2\text{O}_3 + 6\text{H}_2\text{O}$
Chlorides.....	$\text{ErCl}_3$	$\text{YbCl}_3 + 3\text{H}_2\text{O}$
Bromides.....	$\text{ErBr}_3 + 9\text{H}_2\text{O}$	
Iodide.....	$\text{ErI}_3$	
Fluoride.....	$\text{ErF}_3$	
Chlorate.....	$\text{Er}(\text{ClO}_3)_3 + 8\text{H}_2\text{O}$	
Perchlorate.....	$\text{Er}(\text{ClO}_4)_3 + 8\text{H}_2\text{O}$	
Bromate.....	$\text{Er}(\text{BrO}_3)_3 + 9\text{H}_2\text{O}$	
Iodate.....	$\text{Er}(\text{IO}_3)_3 + 3\text{H}_2\text{O}$	
Sulphite.....	$\text{Er}_2(\text{SO}_3)_3 + 3\text{H}_2\text{O}$	
Sulphates.....	$\text{Er}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}$	$\text{Yb}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}$
Double sulphates.....	$\text{Er}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$ $\text{Er}_2(\text{SO}_4)_3 \cdot 5\text{Na}_2\text{SO}_4$ $\text{Er}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4$	
Dithionate.....	$\text{Er}_2(\text{S}_2\text{O}_6)_3 + 18\text{H}_2\text{O}$	
Selenites.....	$\text{Er}_2(\text{SeO}_3)_3 + 5\text{H}_2\text{O}$	$\text{Yb}_2(\text{SeO}_3)_3$
Seleniate.....	$\text{Er}_2(\text{SeO}_4)_3 + 5\text{H}_2\text{O}$	
Nitrate.....	$\text{Er}(\text{NO}_3)_3 + 6\text{H}_2\text{O}$	
Phosphate.....	$\text{ErPO}_4 + \text{H}_2\text{O}$	
Pyrophosphate.....	$\text{Er}_2\text{H}_2(\text{P}_2\text{O}_7)_3 + 7\text{H}_2\text{O}$	
Carbonate.....	$\text{Er}_2\text{O}_3 \cdot 2\text{CO}_2 + 2\text{H}_2\text{O}$	
Oxalates.....	$\text{Er}_2(\text{C}_2\text{O}_4)_3 + 12\text{H}_2\text{O}$	$\text{Yb}_2(\text{C}_2\text{O}_4)_3 + 10\text{H}_2\text{O}$
Acetates.....	$\text{Er}(\text{C}_2\text{H}_3\text{O}_2)_3 + 2\text{H}_2\text{O}$	$\text{Yb}(\text{C}_2\text{H}_3\text{O}_2)_3 + 2\text{H}_2\text{O}$
Sulphide.....	$\text{Er}_2\text{S}_3$	

**Compounds. A. Typical forms.** In the table on this page are given typical compounds of erbium and ytterbium.

**B. Characteristics.** In general chemical behavior the compounds of the yttrium earths resemble closely those of yttrium. The salts of erbium are of a rosy tint and give absorption bands. The oxide is yellowish. Ytterbium forms colorless compounds and gives no absorption bands. The compounds of holmium, thulium, dysprosium, europium, and victorium have not been sufficiently investigated to warrant description. The identification of members of this group is made by the methods of spectrum analysis.

**Separation.** For the separation of erbium from the other members of the yttrium group Methods 8, 9, 11, 12, 13, 20, 26(a), and 28 (page 43) are used. James obtains erbium by his bromate process (*vid.* Separation of Yttrium, page 48) in the fraction between yttrium and thulium.

In separating ytterbium, Methods 8, 9, 11, 21, 26(a), and 28 are recommended. In the bromate process this earth is to be found in the mother liquor after the separation of the fractions containing the other members of the group.

Holmium has been separated by Methods 1, 11, 13, 26(a), and 28. It is found in the bromate process in the fraction between dysprosium and yttrium.

For thulium Methods 8, 25(b), and 28 have been recommended. It crystallizes in the bromate process in the last fraction following the erbium.

Dysprosium has been separated by Methods 11, 26(a), and 28. The bromate of this earth crystallizes between terbium and holmium.

Methods 26 (c) and (d) have been especially effective in separating europium. James finds the main portion of the europium with the cerium earths, especially samarium, after the treatment with sodium sulphate. When lanthanum, praseodymium, neodymium, samarium, europium, and gadolinium are subjected to fractional crystallization as the double magnesium nitrates, europium appears in the last fraction before gadolinium and following samarium.

Methods 8, 21, and 26(a) have been used in separating victorium. Crookes finds that its oxalate is precipitated in nitric acid solution after terbium and before yttrium.

## II. THE TERBIUM GROUP.

### 1. TERBIUM, Tr, 159

### 2. GADOLINIUM, Gd, 156

**Discovery.** Terbium was first isolated by Mosander in 1843 (*vid.* Discovery of Erbium).

In 1886 Marignac and Lecoq de Boisbaudran (Compt. rend. CII, 902) separated from terbium earth the oxide of an unknown element named by them Gadolinium.

**Occurrence.** These earths are found in small quantities associated with the yttrium earths (*vid.* Occurrence of Rare

Earths, page 35). The chief sources of terbium are gadolinite, samarskite, euxenite, and monazite; of gadolinium, samarskite and orthite.

**Extraction.** These earths are extracted from minerals with the members of the yttrium group (*vid.* Extraction of Yttrium, page 46).

**Compounds.** A. *Typical forms.* The following are typical compounds of terbium and gadolinium:

	Tr	Gd
Oxide.....	$\text{Tr}_2\text{O}_3$	
Hydroxide.....	$\text{Tr}_2\text{O}_3 + 6\text{H}_2\text{O}$	
Chloride.....		$\text{GdCl}_3 + 6\text{H}_2\text{O}$
Bromide.....		$\text{GdBr}_3 + 6\text{H}_2\text{O}$
Sulphate.....	$\text{Tr}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}$	
Double sulphate.....		$\text{Gd}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$
Nitrates.....	$\text{Tr}(\text{NO}_3)_3 + 6\text{H}_2\text{O}$	$\text{Gd}(\text{NO}_3)_3 + 5\text{H}_2\text{O}$
Double nitrate.....		$2\text{Gd}(\text{NO}_3)_3 \cdot 3\text{Ni}(\text{NO}_3)_2 + 24\text{H}_2\text{O}$
Carbonates.....	$\text{Tr}_2(\text{CO}_3)_3 + x\text{H}_2\text{O}$	$\text{Gd}_2(\text{CO}_3)_3 + 13\text{H}_2\text{O}$
Acetates.....	$\text{Tr}(\text{C}_2\text{H}_3\text{O}_2)_3$	$\text{Gd}(\text{C}_2\text{H}_3\text{O}_2)_3 + 4\text{H}_2\text{O}$

**B. Characteristics.** The compounds of the terbium earths are very similar in chemical form and behavior to those of the yttrium earths. The members of this group are distinguished from the yttrium earths, with the exception of europium and victorium, on the one hand, and from the cerium earths on the other, in that their double potassium sulphates are more insoluble in a saturated solution of potassium sulphate than the corresponding salts of the former group, and less insoluble than those of the latter.

**Separation.** Methods 8, 11, 18, 19, 26 (a), and 28 (page 43) have been used in separating terbium from other rare earths. James separates terbium from the cerium earths by saturation with sodium sulphate. On conversion of the yttrium earths together with terbium into the bromates, and crystallization, the terbium separates in the first fraction. Gadolinium has been separated by Methods 11, 23, 26(a), (b), (c), (d), and 29. James classifies it in the cerium

group, and by crystallization of the double magnesium nitrates separates it in the last fraction.

### III. THE CERIUM GROUP.

#### 1. CERIUM, Ce, 140.25.

**Discovery.** In the course of the analysis of a mineral from Riddarhyttan, Sweden, in 1803, Klaproth discovered an earth which, while resembling yttria in many of its reactions, differed from it in being insoluble in carbonate of ammonium, and in acquiring, when ignited, a light brown color. Because of this latter peculiarity, the name Ochroite suggested itself to him, from *ὀχρός*, *yellow brown* (Phil. Mag. xix, 95). At the same time, and independently of Klaproth, Berzelius and Hisinger made the same discovery. Their name for the new element was Cerium, chosen in honor of the discovery of the planet Ceres by Piazzi in 1801 (Phil. Mag. xx, 155; xxii, 193).

**Occurrence.** Cerium is found in many minerals, associated, usually, with other members of the rare earth group (*vid.* Occurrence of Rare Earths, page 35). Its chief sources are allanite, monazite, and cerite.

**Extraction.** Cerium is generally extracted from cerite through decomposition of the mineral by heating it with strong sulphuric acid (*vid.* Experiment 1). The decomposition may be accomplished also by the action of a mixture of strong hydrochloric and nitric acids, but better results may be expected by the former method.

**The Element.** *A. Preparation.* Elementary cerium may be obtained (1) by reducing the chloride with sodium or potassium (Mosander); (2) by subjecting the double chloride of cerium and sodium to electrolysis (Pogg. Annal. clv, 633).

*B. Properties.* In appearance cerium resembles iron. While fairly stable in dry air, it oxidizes quickly in moist air. It takes fire more easily than magnesium, and melts at a

lower temperature than silver and at a higher temperature than antimony. It is soluble in dilute acids, but is not attacked by concentrated sulphuric or nitric acid. It combines with chlorine, bromine, and iodine, forming salts. Its specific gravity is 6.6.

**Compounds.** *A. Typical forms.* The following are typical forms of the two classes of cerium compounds:

Oxides. ....	$\text{Ce}_2\text{O}_3$	$\text{CeO}_2$
Hydroxides. ....	$\text{Ce}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$	$2\text{CeO}_2 \cdot 3\text{H}_2\text{O}$
Carbonates. ....	$\text{Ce}_2(\text{CO}_3)_3 + 5\text{H}_2\text{O}$	$\text{Ce}(\text{CO}_3)_2 + 0.5\text{H}_2\text{O}$
Chloride. ....	$\text{CeCl}_3$	
Bromide. ....	$\text{CeBr}_3$	
Iodide. ....	$\text{CeI}_3$	
Perchlorate. ....	$\text{Ce}(\text{ClO}_4)_3 + 8\text{H}_2\text{O}$	
Bromate. ....	$\text{Ce}(\text{BrO}_3)_3 + 9\text{H}_2\text{O}$	
Iodate. ....	$\text{Ce}(\text{IO}_3)_3 + 2\text{H}_2\text{O}$	
Fluorides. ....	$\text{CeF}_3$	$\text{CeF}_4 + \text{H}_2\text{O}$
Cyanide. ....	$\text{Ce}(\text{CN})_3$	
Ferrocyanides. ..	$\text{Ce}_4(\text{FeC}_6\text{N}_6)_3 + 30\text{H}_2\text{O}$	
	$\text{CeKFeC}_6\text{N}_6 + 3\text{H}_2\text{O}$	
Ferricyanide. ....	$\text{CeFeC}_6\text{N}_6 + 8\text{H}_2\text{O}$	
Sulphocyanide ..	$\text{Ce}(\text{CSN})_3 + 7\text{H}_2\text{O}$	
Sulphide. ....	$\text{Ce}_2\text{S}_3$	
Sulphite. ....	$\text{Ce}_2(\text{SO}_3)_3 + 3\text{H}_2\text{O}$	
Sulphates. ....	$\text{Ce}_2(\text{SO}_4)_3 + 3, 5, 6, 8, 9, \text{ and } 12\text{H}_2\text{O}$	$\text{Ce}(\text{SO}_4)_2 + 4\text{H}_2\text{O}$
Double sulphates.	$\text{Ce}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$	$\text{Ce}(\text{SO}_4)_2 \cdot 2\text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$
	$\text{Ce}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$	
	$\text{Ce}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 + 8\text{H}_2\text{O}$	
Nitrates. ....	$\text{Ce}(\text{NO}_3)_3 + 6\text{H}_2\text{O}$	$\text{Ce}(\text{NO}_3)_4$
Double nitrates. .	$\text{Ce}_2(\text{NO}_3)_6 \cdot 3\text{Zn}(\text{NO}_3)_2 + 24\text{H}_2\text{O}$	$2\text{Ce}(\text{NO}_3)_4 \cdot 4\text{KNO}_3 + 3\text{H}_2\text{O}$
	$\text{Ce}_2(\text{NO}_3)_6 \cdot 3\text{Co}(\text{NO}_3)_2 + 24\text{H}_2\text{O, etc.}$	$2\text{Ce}(\text{NO}_3)_4 \cdot 4(\text{NH}_4)\text{NO}_3 + 3\text{H}_2\text{O}$
Phosphates. ....	$\text{CePO}_4$	$(\text{CeO}_2)_4 \cdot (\text{P}_2\text{O}_5)_6 + 26\text{H}_2\text{O}$
Oxalate. ....	$\text{Ce}_2(\text{C}_2\text{O}_4)_3$	
Carbide. ....		$\text{CeC}_2$

*B. Characteristics.* Cerium exists in compounds in two conditions of oxidation. The higher or ceric salts are easily reduced to the lower or cerous condition by the ordinary reducing agents (e.g.  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{C}_2\text{O}_4$ , etc.),



and the cerous salts may be oxidized to the ceric condition by oxidizing agents (e.g.  $\text{PbO}_2 + \text{HNO}_3$ ,  $\text{H}_2\text{O}_2$  in alkaline solution,  $\text{KMnO}_4$ , etc.). In general the cerous salts are colorless, and the ceric yellow. The lower oxide of cerium, ( $\text{Ce}_2\text{O}_3$ ), on ignition goes over to the higher condition, ( $\text{CeO}_2$ ). The cerous salts are the more stable, and consequently they form the greater number. They resemble the yttrium salts in many of their reactions, and are distinguishable from them chiefly by the greater insolubility of the double sulphates with sodium sulphate and potassium sulphate respectively in excess of the alkali sulphate, by the comparative insolubility of the carbonate in ammonium carbonate, and by the possibility of oxidation to a higher condition. Solutions of pure cerium salts give no absorption bands.

**Estimation.** *A. Gravimetric.* Cerium is usually determined gravimetrically as the dioxide, ( $\text{CeO}_2$ ), obtained by the ignition of the hydroxide or the oxalate.

*B. Volumetric.* (1) When ceric oxide, ( $\text{CeO}_2$ ), is treated with hydrochloric acid in the presence of potassium iodide, iodine is set free, according to the following equation:

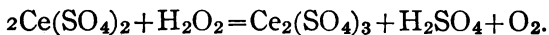


The iodine may be estimated in acid solution by standard thiosulphate, or in alkaline solution by standard arsenious acid (Bunsen, *Ann. Chem. Pharm.* cv, 49; Browning, *Amer. Jour. Sci.* [4] viii, 451).

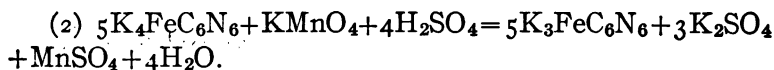
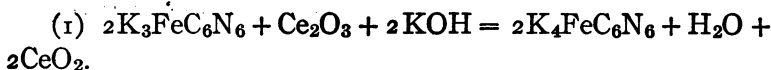
(2) When cerium oxalate is dissolved in sulphuric acid the oxalic acid may be readily determined by potassium permanganate, and the amount of cerium present may be thus estimated (Stolba, *Zeitsch. anal. Chem.* xix, 194; Browning, *Amer. Jour. Sci.* [4] viii, 457).

(3) When yellow ceric compounds are treated with hydrogen dioxide in acid solution, they are reduced to

cerous compounds, with bleaching of color (Knorre, *Zeitsch. angew. Chem.* (1897), 685):



(4) Cerium may be estimated in the presence of the other rare earths by precipitating the hydroxide in the presence of potassium ferricyanide, filtering, and estimating by potassium permanganate the ferrocyanide formed (Browning and Palmer, *Amer. Jour. Sci.* xxvi (1908), 83), according to the equations:

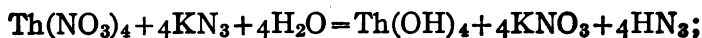


**Separation.** Cerium falls into the analytical group with aluminum, iron, etc. Together with the other rare earths it may be separated from these by oxalic acid or oxalate of ammonium. For separation from the yttrium earths, *vid.* page 48.

Cerium may be separated from lanthanum, praseodymium, and neodymium by the following methods: (1) by treating the hydroxides suspended in a solution of caustic potash with chlorine gas (Mosander, *J. pr. Chem.* xxx, 267), or with liquid bromine (Browning and Roberts, *Amer. Jour. Sci.* xxix, 45); (2) by boiling a solution of the nitrates with potassium bromate in presence of a lump of marble, thus precipitating basic ceric nitrate (James and Pratt, *Jour. Amer. Chem. Soc.* xxxiii, 1326); (3) by treating a solution of the cerium earths with sodium peroxide and boiling (O. N. Witt, *Chem. Ind.* (1896), II, 19); (4) by treating the oxalates of the cerium earths with warm dilute nitric acid, thus separating the cerium as basic nitrate

(Auer von Welsbach, Monatshefte f. Chem. v, 508); (5) by treating a solution of the salts with hydrogen dioxide in the presence of magnesium acetate (Meyer and Koss, Ber. Dtsch. chem. Ges. xxxv, 672); (6) by treating the neutralized nitrate solution with an excess of zinc oxide and adding potassium permanganate, thus precipitating cerium peroxide; (7) by the action of chromic acid on the hydroxides, dissolving the cerium (Esposito, Proc. Chem. Soc. xxii, 20).

From thorium cerium may be separated (1) by repeated precipitations on boiling with sodium thiosulphate (Fresenius and Hintz, Zeitsch. anal. Chem. xxxv, 543); (2) by boiling with potassium trinitride (Dennis and Kortright, Amer. Chem. Jour. xvi, 79):



(3) by boiling a nearly neutral solution of the chlorides with copper and cuprous oxide (Lecoq de Boisbaudran, Compt. rend. xcix, 525); (4) by the action of fumaric acid in 40% alcohol upon solutions of the salts in 40% alcohol (Metzger, Jour. Amer. Chem. Soc. xxiv, 901); (5) by oxidizing cerous salts to the ceric condition and treating with ammonium oxalate, cerium not being precipitated at first (Orlow, Chem. Ztg. xxx, 733). In all of these methods the thorium is precipitated.

Cerium is separated from zirconium by fusion of the oxides with acid potassium fluoride, and extraction with water and a little hydrofluoric acid; the potassium fluo-zirconate is dissolved, and the thorium and cerium remain\* (Delafontaine, Chem. News Lxxv, 230).

In addition to the foregoing, Methods 1, 3, 4, 6-10, 18,

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\* For the action of organic bases as precipitants of the rare earths, *vid.* Jefferson, Jour. Amer. Chem. Soc. xxiv, 540; Baskerville, Science, New Series, xvi, 215; Kolb, J. pr. Chem. [2] Lxvi, 59; Allen, Jour. Amer. Chem. Soc. xxv, 421; Holmberg, Chem. Zentral. 1906, II, 1595.

and 26(b), page 43, have been used in separating cerium from its associates.

**Experimental Work.** *Vid.* end of the chapter.

- |                            |                        |
|----------------------------|------------------------|
| 2. LANTHANUM, La, 139      | 5. SAMARIUM, Sm, 150.4 |
| 3. NEODYMIUM, Nd, 144.3    | 6. SCANDIUM, Sc, 44.1  |
| 4. PRASEODYMIUM, Pr, 140.6 | 7. DECIPIUM, Dp, 171   |

**Discovery.** In 1839 Mosander found that when the nitrate of cerium had been ignited, he was able to extract from it by very dilute acid an earth which differed in properties from that of cerium, while from the portion remaining undissolved he obtained the reactions of the cerium earth. He supposed the unknown substance of the newly discovered earth to be an element, and named it Lanthanum, from *λανθάνειν*, to *hide* (Pogg. Annal. XLVI, 648; Liebig, Annal. XXXII, 235).

In 1841, while engaged in further work upon the extraction of mixtures of cerium and lanthanum oxides by dilute nitric acid, he succeeded in separating from the lanthanum oxide another earth, rosy in color, going over to dark brown on being heated. Reserving for the residual oxide the original name Lanthanum earth, he called the base of the new oxide Didymium, from *δίδυμος*, *twin*,—a name suggested by its close relationship to lanthanum and its almost invariable occurrence with it (Pogg. Annal. LVI, 503).

In 1885 Auer von Welsbach announced that by long-continued fractional crystallization of the double nitrates of ammonium with lanthanum and didymium in the presence of strong nitric acid, he had separated didymium into two elements (Sitzungsber. d. k. Acad. d. Wiss. (1885) XCII, Heft I, II, 317; Ber. Dtsch. chem. Ges. XVIII, 605). The lanthanum crystallized out first, and afterward the decomposition of the didymium took place. To these new elements he gave the names Praseodymium (*πράσινος*, *leek-green*) and Neodymium (*νέος*, *new*).

In 1888 Krüss and Nilson stated, as the result of their work on the absorption spectrum of didymium, that they had discovered indications of the presence of no less than eight elements (Ber. Dtsch. chem. Ges. xx, 2134, 3067). These results, however, have not as yet been confirmed. At the present time the existence of praseodymium and neodymium is accepted.

In 1878 Delafontaine (Compt. rend. LXXXVII, 559, 632) announced the discovery of Decipium in a North Carolina samarskite.

In 1879 Nilson (Ber. Dtsch. chem. Ges. xii, 554), while engaged in extracting ytterbium from euxenite, separated an earth of much lower atomic weight, the unknown element of which he called Scandium.\* The same year Lecoq de Boisbaudran (Compt. rend. LXXXVIII, 323), in the course of an examination of the absorption spectra of the earths separated from samarskite, isolated the earth of another new element, Samarium.

**Occurrence.** The cerium earths occur closely associated with cerium. The following are some of the chief sources: of lanthanum, cerite, allanite, monazite, bastnaesite, and lanthanite; of praseodymium and neodymium, cerite, allanite, monazite, and bastnaesite; of samarium, samarskite, orthite, cerite, gadolinite, and keilhauite; of scandium, gadolinite, yttrotitanite, euxenite, and keilhauite; of decipium, samarskite.

**Extraction.** In the process of extracting cerium from cerite (*vid.* Experiment 1) the oxalates of the cerium earths are precipitated together.

**The Elements.** I. LANTHANUM. *A. Preparation.* The element lanthanum may be obtained (1) by reducing the chloride with potassium; (2) by subjecting the double chloride of lanthanum and sodium to electrolysis.

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\* The discovery of scandium was predicted by Mendeléeff in 1869 and the hypothetical element was named Ekaboron. To it he gave the atomic weight of 44, and he described the properties of several of its compounds.

*B. Properties.* Lanthanum is a metallic element of a lead-gray color. It decomposes cold water slowly and hot water more rapidly, with the evolution of hydrogen. It oxidizes easily in the air. Its specific gravity is from 6.04 to 6.19.

II. PRASEODYMIUM AND NEODYMIUM. The elements praseodymium and neodymium have been isolated by the electrolysis of the anhydrous chlorides (Muthmann and Weiss, Liebig Ann. CCCXXXI, 46).

III. SAMARIUM, SCANDIUM, AND DECIPIUM. These elements have not been isolated.

**Compounds.** *A. Typical forms.* In the table on the next page are shown typical compounds of the members of the cerium group other than cerium.

*B. Characteristics.* The compounds of the other members of the cerium group are very similar to those of cerium in the cerous condition in their behavior toward chemical reagents. They may be distinguished from the compounds of cerium by the absence of yellow color on the addition of oxidizing agents,—a color characteristic of the higher oxide of cerium. Lanthanum may be distinguished from praseodymium and neodymium by the colorlessness of its salts and by the absence of an absorption spectrum. Didymium salts in general are of a rosy color and give a distinctive absorption spectrum.

Neodymium salts are rose-colored and are very similar in appearance and behavior to the salts of didymium. The oxide  $\text{Nd}_2\text{O}_3$  is bluish. Praseodymium salts are green. While their chemical form resembles closely that of the neodymium salts, higher oxides are definitely known in the case of praseodymium. The ordinary oxide  $\text{Pr}_2\text{O}_3$  is greenish white; the higher oxide  $\text{Pr}_4\text{O}_7$  is nearly black. Each of the two elements has distinctive spectra, spark and absorption. Mixed, the elements give the didymium spectrum. The lower oxide and the salts of samarium are yellow.

Oxides .....	$\text{La}_2\text{O}_3$ .....	$\text{Pr}_2\text{O}_3$ .....	$\text{Nd}_2\text{O}_3$ .....	$\text{Sc}_2\text{O}_3$ *	$\text{Sm}_2\text{O}_3$ $\text{Sm}_4\text{O}_7$ .....	$\text{Dy}_2\text{O}_3$ .....
Hydroxides .....	$\text{La}(\text{OH})_3$ .....	$\text{Pr}_2\text{O}_7$ .....	.....	.....	.....	.....
Chlorides .....	$\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ .....	$\text{Pr}_2\text{O}_7$ .....	.....	$\text{Sc}_2\text{O}_3 + 6\text{H}_2\text{O}$ .....	$\text{Sm}_2\text{O}_3 + 6\text{H}_2\text{O}$ .....	$\text{Dy}_2\text{O}_3 + 6\text{H}_2\text{O}$ .....
Oxychlorides .....	$\text{LaOCl}$ .....	$\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$ .....	$\text{NdCl}_3 + 6\text{H}_2\text{O}$ .....	$\text{ScCl}_3 + 3\text{H}_2\text{O} + 12\text{H}_2\text{O}$ .....	$\text{SmCl}_3 + 6\text{H}_2\text{O}$ .....	.....
Chlorate .....	$\text{La}(\text{ClO}_3)_3$ .....	.....	.....	.....	$\text{Sm OCl}$ .....	.....
Perchlorate .....	$\text{La}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ .....	.....	.....	.....	.....	.....
Bromides .....	$\text{LaBr}_3 \cdot 7\text{H}_2\text{O}$ .....	$\text{PrBr}_3 \cdot 6\text{H}_2\text{O}$ .....	.....	$\text{Sc}_2\text{Br}_3 + 3\text{H}_2\text{O} + 12\text{H}_2\text{O}$ .....	$\text{SmBr}_3 + 6\text{H}_2\text{O}$ .....	.....
Bromate .....	$\text{La}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ .....	.....	.....	.....	.....	.....
Iodide .....	.....	.....	.....	.....	.....	.....
Iodates .....	$\text{La}_2(\text{IO}_3)_4 \cdot 3\text{H}_2\text{O}$ .....	.....	.....	.....	$\text{SmI}_3$ .....	.....
Fluoride .....	$\text{LaF}_3$ .....	.....	$\text{NdF}_3$ .....	.....	$\text{Sm}(\text{IO}_3)_3 + 6\text{H}_2\text{O}$ .....	$\text{Dy}_2(\text{IO}_3)_4 + 6\text{H}_2\text{O}$ .....
Sulphides .....	$\text{La}_2\text{S}_3$ .....	$\text{Pr}_2\text{S}_3$ .....	.....	.....	$\text{SmF}_2 \cdot 0.5\text{H}_2\text{O}$ .....	.....
Sulphites .....	$\text{La}_2(\text{SO}_3)_3 \cdot 4\text{H}_2\text{O}$ .....	$\text{Pr}_2(\text{SO}_3)_3 \cdot 8\text{H}_2\text{O}$ .....	$\text{Nd}_2(\text{SO}_3)_3 + 8\text{H}_2\text{O}$ .....	$\text{Sc}_2(\text{SO}_3)_3$ .....	$\text{Sm}_2\text{S}_4$ .....	.....
Sulphates .....	$\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ .....	$\text{Pr}_2\text{O}_7\text{SO}_4$ .....	$\text{Nd}_2\text{O}_7\text{SO}_4$ .....	$\text{Sc}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}$ .....	$\text{Sm}_2(\text{SO}_3)_3$ .....	$\text{Dy}_2(\text{SO}_4)_3 + 24\text{H}_2\text{O}$ .....
Double sul- phates .....	$\text{La}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$ .....	$\text{Pr}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4 + \text{H}_2\text{O}$ .....	.....	$\text{Sc}_2(\text{SO}_4)_3 + 3\text{K}_2\text{SO}_4$ .....	$\text{Sm}_2(\text{SO}_4)_3 + 9\text{K}_2\text{SO}_4$ .....	.....
.....	$\text{La}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$ .....	$\text{Pr}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 + 8\text{H}_2\text{O}$ .....	.....	$\text{Sc}_2(\text{SO}_4)_3 + 3\text{Na}_2\text{SO}_4$ .....	$\text{Sm}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SO}_4$ .....	.....
Selenites .....	$\text{La}_2(\text{SeO}_3)_3 \cdot 9\text{H}_2\text{O}$ .....	$\text{Pr}_2(\text{SeO}_3)_3 \cdot \text{H}_2\text{SeO}_3 + 3\text{H}_2\text{O}$ .....	.....	$\text{Sc}_2(\text{SeO}_3)_3 + \text{H}_2\text{O}$ .....	$\text{Sm}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4$ .....	.....
Seleniates .....	$\text{La}_2(\text{SeO}_4)_3 \cdot 6\text{H}_2\text{O}$ .....	$\text{Pr}_2(\text{SeO}_4)_3 + 8\text{H}_2\text{O}$ .....	.....	.....	$\text{Sm}_2(\text{SeO}_4)_3 + 8\text{H}_2\text{O}$ .....	.....
Double sele- nates .....	$\text{La}_2(\text{SeO}_4)_3 \cdot \text{K}_2\text{SeO}_4 + 9\text{H}_2\text{O}$ .....	$\text{Pr}_2(\text{SeO}_4)_3 \cdot \text{K}_2\text{SeO}_4 + 4\text{H}_2\text{O}$ .....	.....	.....	.....	.....
.....	$\text{La}_2(\text{SeO}_4)_3 \cdot \text{Na}_2\text{SeO}_4 + 4\text{H}_2\text{O}$ .....	.....	.....	.....	.....	.....
Nitrates .....	$\text{La}_2(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ .....	$\text{Pr}_2(\text{NO}_3)_3 + 6\text{H}_2\text{O}$ .....	$\text{Nd}(\text{NO}_3)_3$ .....	$\text{Sc}(\text{NO}_3)_3$ .....	$\text{Sm}(\text{NO}_3)_3 + 6\text{H}_2\text{O}$ .....	.....
Double ni- trates .....	.....	$\text{Pr}(\text{NO}_3)_3 \cdot 2(\text{NH}_4)\text{NO}_3 + 4\text{H}_2\text{O}$ .....	.....	.....	.....	.....
Phosphates .....	$\text{LaPO}_4$ ; also meta and pyro forms .....	$\text{Pr}(\text{NO}_3)_3 \cdot 2\text{NaNO}_3 + \text{H}_2\text{O}$ .....	.....	.....	.....	.....
Carbonates .....	$\text{La}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ .....	$\text{Pr}_2(\text{CO}_3)_3 + 8\text{H}_2\text{O}$ .....	.....	$\text{Sc}_2(\text{CO}_3)_3 + 12\text{H}_2\text{O}$ .....	$\text{SmPO}_4$ .....	.....
Oxalates .....	$\text{La}_2(\text{C}_2\text{O}_4)_3$ .....	$\text{Pr}_2(\text{C}_2\text{O}_4)_3 + 10\text{H}_2\text{O}$ .....	.....	$\text{Sc}_2(\text{C}_2\text{O}_4)_3 + 6\text{H}_2\text{O}$ .....	$\text{Sm}_2(\text{C}_2\text{O}_4)_3 + 3\text{H}_2\text{O}$ .....	$\text{Dy}_2(\text{C}_2\text{O}_4)_3 + 12\text{H}_2\text{O}$ .....
.....	.....	.....	.....	.....	$\text{Sm}_2(\text{C}_2\text{O}_4)_3 + 10\text{H}_2\text{O}$ .....	.....

\* Crookes (Proc. Roy. Soc. (London), (A) LXXX, 516, and LXXXIV, 79) has prepared a large number of salts of scandium; many of them are salts of organic acids and are basic.

Solutions of the salts give characteristic absorption bands. The oxides and salts of scandium and decipium are colorless. The salts show no absorption spectrum.

**Estimation.** Like cerium, the other members of its group are generally estimated as oxides, obtained by ignition of the hydroxides or oxalates.

**Separation.** *A. Lanthanum from didymium.* Lanthanum may be separated from didymium (1) by dissolving the sulphates in water at 9° C. and gradually raising the temperature,—the lanthanum sulphate separating first (Hermann, J. pr. Chem. LXXXII, 385); (2) by heating the nitrates at 400°–500° C. and extracting with water,—the didymium tending to form an insoluble basic nitrate (Damour and Deville, Bull. Soc. Chim. d. Paris, II, 339); (3) by dissolving half of a given amount of the oxides in warm dilute nitric acid, then adding the other half, with constant stirring, cooling the mass, and extracting with water (*vid.* Experiment 1),—the didymium being found in the residue (Auer von Welsbach, Monatshefte f. Chem. v, 508); (4) by fractional crystallization of the double magnesium nitrates,—the lanthanum appearing in the first crystallizations (James, Jour. Amer. Chem. Soc. xxx, 979).

Separation Methods 1, 9, 11, 12, 17–23, 25(b), and 26(a), (b), and (c), page 43, have also been used in separating lanthanum.

*B. Praseodymium from neodymium.* Didymium may be separated into its two constituents (1) by making several hundred fractional crystallizations, first of the double nitrate of ammonium and didymium and later of the double nitrate of sodium and didymium, in the presence of lanthanum and nitric acid,—the neodymium salt being the more soluble (Auer von Welsbach, Sitzungsber. d. k. Acad. d. Wiss. (1885) xcii, Heft I, II, 317); (2) by allowing nitric acid to act upon the oxalates,—the praseodymium salt being the more soluble (Scheele, Ber. Dtsch. chem. Ges. xxxii, 417);



(3) by treating the sulphates with water,—the praseodymium sulphate being the more soluble (Muthmann and Rölzig, Ber. Dtsch. chem. Ges. xxxi, 1718); (4) by making fractional precipitations of a solution of didymium nitrate by means of sodium acetate and hydrogen peroxide,—the praseodymium separating first (Meyer and Koss, Ber. Dtsch. chem. Ges. xxxv, 676); (5) by making fractional crystallizations of the double magnesium nitrates,—the praseodymium appearing first after the lanthanum (*vid.* (4), Separation of Lanthanum from Didymium). Methods 1, 8(a), 9, 11, 12, 19, 22, 23, and 26(a), page 43, have also been used in the separation of praseodymium and neodymium from their associates and from each other.

Samarium, together with gadolinium and europium, is found by James in the mother liquors obtained during the fractionation of the double magnesium nitrates of lanthanum, praseodymium, and neodymium. Urbain and Lacombe (Compt. rend. cxxxvii, 792, and cxxxviii, 84) have found that the addition of bismuth-magnesium nitrate helps in the separation. The samarium appears in the least soluble fractions. *Vid.* also Methods 9, 11, 20, 23, and 26(a), (b), and (d), page 43.

Scandium is obtained with ytterbium by James in the mother liquors from the bromate crystallizations (*vid.* diagram, page 213.) It is separated from ytterbium by precipitation as the double potassium sulphate. *Vid.* also Methods 8 and 21, page 43.

Decipium may be separated from the terbium earths by fractional precipitation with potassium sulphate. The double sulphate of decipium and potassium is among the most soluble double potassium sulphates of the cerium group, but is less soluble than the corresponding salts of the yttrium and terbium groups. *Vid.* also Methods 8, 11, 20, and 22, page 43.

## EXPERIMENTAL WORK ON CERIUM, LANTHANUM, PRASEODYMIUM, AND NEODYMIUM.

*Experiment 1. Extraction of cerium, lanthanum, and didymium salts from cerite or monazite.* Treat 25 grm. of the powdered mineral with common sulphuric acid and stir until the mass has the consistency of thick paste. Heat until the excess of sulphuric acid is removed. Cool, pulverize, and digest with cold water until no further precipitate appears upon the addition of ammonium oxalate to a few drops of the extract. Pass hydrogen sulphide into the solution to remove traces of bismuth and copper. Filter, and to the filtrate add oxalic acid to complete precipitation of the oxalates of cerium, lanthanum, and didymium. Ignite the oxalates, and dissolve in hydrochloric acid the oxides obtained; or, convert the oxalates to nitrates by treating with nitric acid. To the solution add potassium hydroxide until the precipitation of the hydroxides is complete. Make up the volume of the liquid in which the hydroxides are suspended to about 200 cm.<sup>3</sup> Add about 5 grm. of potassium hydroxide to insure an excess, and pass a slow current of chlorine gas through, stirring from time to time, until the liquid is no longer alkaline in reaction and the precipitate has assumed a deep-yellow color.\* By this process the cerium hydroxide is oxidized to the dioxide, which remains undissolved, and the lanthanum and didymium hydroxides are dissolved. When the separation is complete, a portion of the washed precipitate dissolved in hydrochloric acid should give no evidence of the presence of didymium,—for example, no absorption spectrum (*vid. Experiment 12*). The absence of didymium at this point is considered sufficient evidence of the absence of lanthanum. To the solution containing the lanthanum and didymium,

\* The processes of James and Pratt, which use potassium bromate and marble, or of Browning and Roberts, which substitute bromine for chlorine, may be employed for the separation. *Vid.* page 59.

the cerium dioxide having been removed by filtration, add oxalic acid until the precipitation is complete. Filter off the oxalates, wash, dry, and ignite. Dissolve one half of the oxides obtained by this process in the least possible amount of warm, dilute nitric acid, and add the remainder of the oxides to the solution. Stir thoroughly, and when the mass is cool extract with water. The didymium tends to be in the residue and the lanthanum in solution.

*Experiment 2. Reduction and oxidation of cerium compounds.* (a) To a small portion of the carefully washed cerium dioxide obtained in the previous experiment add a little hydrochloric acid diluted with an equal volume of water and boil. Note the evolution of chlorine and the ultimate colorless solution of cerium chloride, ( $\text{CeCl}_3$ ).

(b) To a portion of the solution obtained in (a) add a few drops of ammonium hydroxide in excess and some hydrogen dioxide. Note the orange to red-brown precipitate ( $\text{CeO}_3?$ ). Other oxidizing agents, such as sodium hypochlorite, sodium peroxide, lead dioxide, potassium permanganate, etc., may be used. Boil the solution holding the precipitate in suspension and note that the deep-yellow color changes to a lighter yellow. The precipitate becomes essentially the dioxide, ( $\text{CeO}_2$ ).

(c) To another portion of the washed cerium dioxide from Experiment 1 ( $2\text{CeO}_2 \cdot 3\text{H}_2\text{O}$ ) add hydrochloric acid as before, and also a crystal of potassium iodide in the cold. Note the liberation of iodine according to the reaction  $2\text{CeO}_2 + 8\text{HCl} + 2\text{KI} = 2\text{CeCl}_3 + 2\text{KCl} + \text{I}_2 + 4\text{H}_2\text{O}$ .

*Experiment 3. Formation of ceric nitrate, ( $\text{Ce}(\text{NO}_3)_4$ ).* Dissolve in nitric acid a portion of the hydrated ceric oxide formed in Experiment 1. Note the orange-red color.

Try the action of hydrogen dioxide and oxalic acid upon separate portions of the solution.

*Experiment 4. Precipitation of cerous hydroxide, ( $\text{Ce}(\text{OH})_3$ ).* (a) To a solution of cerium chloride add

sodium, potassium, or ammonium hydroxide in solution. Note the insolubility of the hydroxide in excess of these reagents.

(b) Repeat the experiment with tartaric acid present in the solution.

*Experiment 5. Precipitation of cerous carbonate,  $(\text{Ce}_2(\text{CO}_3)_3)$ .* (a) To a solution of cerium chloride add a solution of sodium or potassium carbonate. Note the comparative insolubility in excess.

(b) Repeat the experiment, using ammonium carbonate as the precipitant.

(c) Try the action of the common acids upon the carbonate of cerium.

*Experiment 6. Precipitation of cerium oxalate,  $(\text{Ce}_2(\text{C}_2\text{O}_4)_3)$ .* (a) To a solution of a cerium salt add oxalic acid or an oxalate. Note the crystalline character of the precipitate, especially after the liquid has been stirred and boiled.

(b) Try the action of hydrochloric acid upon cerium oxalate.

*Experiment 7. Precipitation of the double sulphate of cerium and potassium or sodium,  $(\text{Ce}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$  or  $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SO}_4$ ).* To a few drops of a concentrated solution of a cerous salt add a small portion of a saturated solution of sodium or potassium sulphate.

*Experiment 8. Precipitation of cerium phosphate,  $(\text{CePO}_4)$ .*

(a) To a solution of a cerous salt add sodium phosphate in solution.

(b) Try the action of hydrochloric and acetic acids upon separate portions of the precipitate.

*Experiment 9. Precipitation of cerous fluoride,  $(\text{CeF}_3)$ .* To a solution of cerium chloride add potassium fluoride in solution.

*Experiment 10. Precipitation of the ferrocyanide of cerium,  $(\text{Ce}_4(\text{FeC}_6\text{N}_6)_3)$ .* (a) To a solution of cerium chloride add potassium ferrocyanide.

(b) Note that potassium ferricyanide gives no precipitate.

*Experiment 11. Comparison of lanthanum and didymium with cerium.* (a) Perform Experiments 4 to 10 inclusive upon dilute solutions of lanthanum and didymium salts.

(b) Note that pure lanthanum and didymium salts give no change of color with oxidizing agents. Compare with cerium salts (*vid.* Experiment 2).

*Experiment 12. Didymium absorption spectrum.* Place a solution of a didymium salt between the slit of the spectroscope and a luminous flame. Note the dark bands. Observe that cerium and lanthanum salts in solution show no absorption bands when free from didymium.

*Experiment 13. Separation of praseodymium and neodymium.* If time and material allow, an interesting experiment may be performed by taking about 100 grm. of the oxides of lanthanum and didymium (praseodymium and neodymium), dissolving them in a known amount of nitric acid, neutralizing an equal amount of nitric acid by means of magnesium oxide, mixing the two solutions, and proceeding with the fractional crystallization of the double nitrates to the point where change of color indicates the separation of praseodymium and neodymium. Observe the differences in the absorption bands.

*Experiment 14. Negative test of the salts of cerium, lanthanum and didymium.* Note that hydrogen sulphide gives no precipitate with salts of this group. Ammonium sulphide precipitates the hydroxides, not the sulphides.

#### IV. THORIUM.\* Th. 232.5.

**Discovery.** As early as the year 1818 Berzelius, working on a mineral from Fahlun, Sweden, believed that he had discovered a new earth (*Annal. der Phys. u. Chem.* (1818))

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\* For a discussion of radio active properties, see Chapter III.

xxix, 247). He gave it the name Thoria, from Thor, son of the Scandinavian war god Odin. Some years later, however, he identified the supposed new earth as chiefly a basic phosphate of yttrium (Pogg. Annal. iv, 145). In 1828 Esmark discovered, near Brevig, Norway, the mineral since known as thorite. From it Berzelius isolated an unknown earth; its similarity to the substance described by him some ten years earlier prompted the name Thoria (Pogg. Annal. xvi, 385).

**Occurrence.** Thorium is found in combination in certain rare minerals (*vid.* Occurrence of Rare Earths, page 35). Its chief sources are monazite, thorianite, and thorite.

**Extraction.** Two common methods for the extraction of thorium salts are here indicated:

(1) *From thorite.* The mineral is decomposed by heating it with sulphuric acid (*vid.* Cerium, Experiment 1, page 67). After the extraction of the sulphate with cold water, the solution is heated to 100° C. and an impure sulphate of thorium comes down. By repeated solution of the precipitate in cold water and reprecipitation by means of heat a pure sulphate is finally obtained (Delafontaine, Ann. Chem. Pharm. cxxxi, 100).

(2) *From monazite.* The mineral is decomposed by sulphuric acid and the oxalates are precipitated by oxalic acid (*vid.* Experiment 1).

**The Element.** *A. Preparation.* Elementary thorium may be obtained (1) by heating the double chloride of thorium and potassium with metallic sodium (Nilson); (2) by reducing the double fluoride of potassium and thorium with potassium; (3) by reducing with aluminum.

*B. Properties.* Thorium is known in two forms, (1) that of a grayish, glistening powder, and (2) crystalline. It is stable in the air, and does not decompose water, even at 100° C. When heated in a current of chlorine, bromine, or iodine it glows and forms the salt. It is soluble in

dilute hydrochloric and sulphuric acids, in concentrated sulphuric acid with the liberation of sulphur dioxide, and in aqua regia. It is acted upon very slowly by nitric acid, and is not attacked by the alkali hydroxides. The specific gravity of thorium in the amorphous condition is 10.97; in crystalline form 11.2.

**Compounds.** *A. Typical forms.* The following are typical compounds of thorium:

Oxides,  $\text{ThO}_2$ ;  $\text{Th}_2\text{O}_7$ .

Hydroxide,  $\text{Th}(\text{OH})_4$ .

Chlorides,  $\text{ThCl}_4$ ; also double salts with  $\text{KCl}$  and  $\text{NH}_4\text{Cl}$ .

Oxychloride,  $\text{ThOCl}$ .

Bromide,  $\text{ThBr}_4$ .

Iodide,  $\text{ThI}_4$ .

Fluoride,  $\text{ThF}_4 + 4\text{H}_2\text{O}$ .

Chlorate,  $\text{Th}(\text{ClO}_3)_4$ .

Perchlorate,  $\text{Th}(\text{ClO}_4)_4$ .

Bromate,  $\text{Th}(\text{BrO}_3)_4$ .

Iodate,  $\text{Th}(\text{IO}_3)_4$ .

Sulphide,  $\text{ThS}_2$ .

Oxysulphide,  $\text{ThOS}$ .

Sulphite,  $\text{Th}(\text{SO}_3)_2 + \text{H}_2\text{O}$ .

Sulphates,  $\text{Th}(\text{SO}_4)_2 + 9\text{H}_2\text{O}$ ; also double salts with  $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ; and  $(\text{NH}_4)_2\text{SO}_4$ .

Selenite,  $\text{Th}(\text{SeO}_3)_2 + \text{H}_2\text{O}$ .

Seleniate,  $\text{Th}(\text{SeO}_4)_2 + 9\text{H}_2\text{O}$ .

Nitrate,  $\text{Th}(\text{NO}_3)_4 + 12\text{H}_2\text{O}$ .

Borides,  $\text{ThB}_4$ ,  $\text{ThB}_6$ .

Phosphate,  $\text{Th}_3(\text{PO}_4)_4 + 4\text{H}_2\text{O}$ .

Pyrophosphate,  $\text{ThP}_2\text{O}_7 + 2\text{H}_2\text{O}$ .

Ferrocyanide,  $\text{ThFe}(\text{CN})_6 + 4\text{H}_2\text{O}$ .

Silicide,\*  $\text{ThSi}$ .

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\* Hönigschmid, *Compt. rend.* CXLII, 157; CXLIII, 224.

Silicate,  $\text{ThSiO}_4$ .

Carbonates,  $\text{Th}(\text{CO}_3)_2$ ;  $\text{Th}(\text{CO}_3)_2 \cdot 3\text{Na}_2\text{CO}_3 + 12\text{H}_2\text{O}$ .

Oxalate,  $\text{Th}(\text{C}_2\text{O}_4)_2 + 2\text{H}_2\text{O}$ .

*B. Characteristics.* The compounds of thorium resemble in chemical form those of cerium in the ceric condition. Thorium resembles cerium also in having a hydroxide insoluble in the alkali hydroxides, and in forming a double sulphate with potassium sulphate, insoluble in excess of that precipitant. The salts of thorium are colorless except where the element is combined with an acid having a color of its own. They are in general insoluble, with the exception of the chloride, the nitrate and the sulphate. Possibly the most distinctive reactions of thorium compounds are the ready formation of a soluble double oxalate when ammonium oxalate is added in excess to a thorium salt in solution, and the precipitation of the hydroxide when a solution of a thorium salt is boiled with potassium hydroxide (Dennis and Kortright, Amer. Chem. Jour. xvi, 79).

*Estimation.* Thorium is ordinarily estimated as the oxide ( $\text{ThO}_2$ ), obtained by ignition of the hydroxide, the nitrate, or the oxalate.

*Separation.* Thorium, together with the rare earths cerium, yttrium, zirconium, etc., may be separated from the other elements by oxalic acid. Methods for its separation from yttrium and cerium have already been given (*vid.* pages 48 and 60), but two recent methods may be mentioned here: (1) the action of potassium iodate in the presence of nitric acid upon rare earth solutions,—the thorium salts remaining insoluble even on boiling (R. J. Meyer, Ztsch. f. anorg. Chem. LXXI, 65), a method especially recommended for separations from scandium; (2) the action of sebacic acid on rare earth solutions,—the thorium sebacate being precipitated (Smith and James, Jour. Amer. Chem. Soc. xxxiv, 281).



From zirconium thorium may be separated (1) by the action of acids upon the potassium double sulphates,—the zirconium salt being the more soluble; (2) by the action of an excess of hydrochloric acid upon the soluble double ammonium oxalates,—the zirconium remaining in solution; (3) by fusion with acid potassium fluoride; (4) by the action of dimethylamine upon solutions of the salts,—thorium hydroxide being precipitated (Kolb, J. pr. Chem. [2] LXVI, 59).

### EXPERIMENTAL WORK ON THORIUM.

*Experiment 1. Extraction of thorium oxide from monazite.* Treat 25 grm. of finely ground monazite with common sulphuric acid, according to the method already described (*vid.* Experiment 1, page 67). Precipitate the oxalates with oxalic acid,—not ammonium oxalate,—boil and filter. Remove the oxalates to a porcelain dish and warm with nitric acid until they are decomposed. Evaporate to dryness to remove excess of nitric acid, dissolve in water, and precipitate thorium thiosulphate with sodium thiosulphate.

Note. This method may be employed for the extraction of thorium from discarded Welsbach-light mantles.

*Experiment 2. Precipitation of thorium hydroxide,  $(\text{Th}(\text{OH})_4)$  and thorium thiosulphate,  $(\text{Th}(\text{S}_2\text{O}_3)_2)$ .* (a) To a solution of a thorium salt add sodium, potassium; or ammonium hydroxide. Note the solubility of the hydroxide in excess of the precipitant.

(b) To a solution of a thorium salt add sodium thiosulphate in solution and boil.

*Experiment 3. Precipitation of thorium carbonate,  $(\text{Th}(\text{CO}_3)_2)$ .* (a) To a solution of a thorium salt add potassium or sodium carbonate. Note the solubility of the precipitate in excess and the reprecipitation on boiling.

(b) Repeat, using ammonium carbonate.

(c) Note the solvent action of the common acids upon thorium carbonate.

*Experiment 4. Precipitation of the oxalate of thorium,  $(\text{Th}(\text{C}_2\text{O}_4)_2 + 2\text{H}_2\text{O})$ .* (a) To a solution of a thorium salt add a solution of oxalic acid. Note the insolubility in excess of the precipitant.

(b) Repeat, using ammonium oxalate as the precipitant. Note the solubility in excess, especially on warming, and the reprecipitation upon the addition of hydrochloric acid.

(c) Try the solvent action of ammonium acetate upon thorium oxalate.

*Experiment 5. Precipitation of the double sulphate of potassium and thorium,  $(\text{Th}(\text{SO}_4)_2 \cdot 2\text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$  or  $\text{Th}(\text{SO}_4)_2 \cdot 4\text{K}_2\text{SO}_4 + 2\text{H}_2\text{O})$ .* Saturate a solution of a thorium salt with potassium sulphate. (The corresponding sodium salt  $(\text{Th}(\text{SO}_4)_2 \cdot \text{Na}_2\text{SO}_4 + 6\text{H}_2\text{O})$  is somewhat soluble in excess of sodium sulphate.)

*Experiment 6. Precipitation of thorium phosphate,  $(\text{Th}_3(\text{PO}_4)_4 + 4\text{H}_2\text{O})$ .* To a solution of a thorium salt add sodium phosphate in solution. Orthophosphoric acid is said to precipitate an acid phosphate  $(\text{ThH}_2(\text{PO}_4)_2)$ .

*Experiment 7. Precipitation of thorium fluoride,  $(\text{ThF}_4 + 4\text{H}_2\text{O})$ .* To a solution of a thorium salt add a solution of potassium fluoride. Double salts with thorium fluoride may also form ( $x\text{KF} \cdot y\text{ThF}_4$  typical).

*Experiment 8. Precipitation of thorium ferrocyanide,  $(\text{ThFe}(\text{CN})_6 + 4\text{H}_2\text{O})$ .* To a solution of a thorium salt add a solution of potassium ferrocyanide. Note the absence of precipitation with potassium ferricyanide.

*Experiment 9. Action of hydrogen peroxide upon salts of thorium.* To a solution of a thorium salt add a little hydrogen peroxide, and warm.

*Experiment 10. Precipitation of thorium iodate,  $(\text{Th}(\text{IO}_3)_4)$ .* To a solution of thorium nitrate add a solu-

tion of potassium iodate. Note the insolubility in fairly strong nitric acid.

*Experiment 11. Precipitation of thorium sebacate.* To a neutral solution of a thorium salt add a hot solution of sebacic acid.

*Experiment 12. Negative test of thorium salts.* To a solution of a thorium salt add hydrogen sulphide. Note that ammonium sulphide precipitates the hydroxide, not the sulphide.

### V. ZIRCONIUM, Zr, 90.6.

**Discovery.** While engaged in the analysis of the zircons, in 1788, Klaproth found one variety containing 31.5% of silica, 0.5% of the oxides of iron and nickel, and 68% of an earth which differed from all earths previously known to him. He observed that it was soluble in the acids, but insoluble in the alkalies, in the latter respect differing from alumina (Ann. de Chim. 1, 238). The fact that zircon was the source of the new earth suggested the name Zirconium for the element.

**Occurrence.** Zirconium is found combined, widely diffused, but always in small quantities (*vid.* Occurrence of Rare Earths, page 35). Its chief source is zircon.

**Extraction.** Zirconium salts may be extracted from zircon by the following methods:

(1) The finely powdered mineral is fused with acid potassium fluoride (*vid.* Experiment 1) (Marignac, Ann. Chim. Phys. [3] LX, 257).

(2) The mineral is fused with potassium bisulphate and the fused mass extracted with dilute boiling sulphuric acid. The basic sulphate ( $3\text{ZrO}_2 \cdot \text{SO}_3$ ) is left as a residue (Franz, Ber. Dtsch. chem. Ges. 11, 58).

(3) The finely powdered mineral is heated with a mixture of sodium hydroxide and sodium fluoride, the mass is cooled, pulverized, and extracted with water. The residue,

which consists mainly of sodium zirconate, is digested with hydrochloric acid until dissolved. After the solution has been evaporated to a small volume the zirconium oxychloride separates in crystalline form (Bailey, Proc. Royal Soc. XLVI, 74).

(4) The finely powdered mineral is fused with sodium carbonate, and the melt, consisting of sodium silicate and sodium zirconate, is extracted with water. The silicate dissolves and the zirconate is hydrolyzed, forming zirconium hydroxide, which, after washing, is dissolved in hydrochloric or sulphuric acid.

**The Element.** *A. Preparation.* Elementary zirconium may be obtained in the amorphous condition (1) by reducing potassium fluozirconate with potassium (Berzelius), and (2) by reducing the oxide with magnesium (Phipson). It may be obtained in crystalline form by heating potassium fluozirconate with aluminum (Troost), and in graphitic form by heating sodium fluozirconate with iron at  $850^{\circ}\text{C}$ .

*B. Properties.* (1) Zirconium in the amorphous condition is a black powder. Heated in the air it burns brightly to the oxide. It oxidizes also when fused with alkali nitrates, carbonates, and chlorates, and is only slightly attacked by acids.

(2) In crystalline form zirconium has much the appearance of antimony. Heated in the air it oxidizes very slowly. It is not acted upon by fusion with alkali nitrates, carbonates, or chlorates, but is soluble in the acids upon the application of heat. The density of the pure metal is 6.4; its melting point is  $2350^{\circ}$  (Weiss).

**Compounds.** *A. Typical forms.* The following are typical compounds of zirconium:

Oxides,  $\text{ZrO}_2$ ;  $\text{ZrO}_3$ .

Hydroxide,  $\text{Zr}(\text{OH})_4$ .

Chlorides,  $\text{ZrCl}_4$ ; also double salts with  $\text{KCl}$  and  $\text{NaCl}$ .  
 Oxyhalides,  $\text{ZrOCl}_2 + 3\text{H}_2\text{O}$ ;  $\text{ZrOBr}_2 + 3\text{H}_2\text{O}$ ;  $\text{ZrI}(\text{OH})_3 + 3\text{H}_2\text{O}$ .  
 Bromide,  $\text{ZrBr}_4$ .  
 Iodide,  $\text{ZrI}_4$ .  
 Fluoride,  $\text{ZrF}_4$ .  
 Oxysulphide,  $\text{ZrOS}$ .  
 Sulphite,  $\text{Zr}(\text{SO}_3)_2$ .  
 Sulphates,  $\text{Zr}(\text{SO}_4)_2 + 4\text{H}_2\text{O}$ ;  $3\text{ZrO}_2 \cdot \text{SO}_3$ .  
 Selenite,  $\text{Zr}(\text{SeO}_3)_2$ .  
 Nitrate,  $\text{Zr}(\text{NO}_3)_4 + 5\text{H}_2\text{O}$ .  
 Phosphate,  $\text{Zr}_3(\text{PO}_4)_4$ .  
 Pyrophosphate,  $\text{ZrP}_2\text{O}_7$ .  
 Carbonate,  $3\text{ZrO}_2 \cdot \text{CO}_2 + 8\text{H}_2\text{O}$ .  
 Oxalates,  $\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot 2\text{Zr}(\text{OH})_4$ ;  $\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot \text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 + 8\text{H}_2\text{O}$ .  
 Zirconates,  $\text{Na}_4\text{ZrO}_4$ ;  $\text{Li}_2\text{ZrO}_3$ , etc.  
 Zirconyl\*-nitric or nitrato-zirconic acid,  $\text{H}_2\text{ZrO}(\text{NO}_3)_4 + 4\text{H}_2\text{O}$ .  
 Zirconyl-sulphuric or sulphato-zirconic acid,  $\text{H}_2\text{ZrO}(\text{SO}_4)_2 + 3\text{H}_2\text{O}$ .  
 Fluozirconate,  $\text{K}_2\text{ZrF}_6$ .  
 Carbide,  $\text{ZrC}$ .  
 Silicide,  $\text{ZrSi}$ .

*B. Characteristics.* In chemical structure the compounds of zirconium bear a strong resemblance to those of thorium, titanium, germanium, and silicon. The oxide, in its behavior as a base toward oxides having more acidic qualities, resembles the oxide of thorium ( $\text{ThO}_2$ ). With the weaker acids, carbonic and oxalic, it shows weaker basic properties in the formation of basic salts. With strong bases it manifests acidic properties, like the oxide of titanium, and forms zirconates (*vid.* Typical Forms,

\* Rosenheim, Ber. Dtsch. chem. Ges. XL, 803, 810; Hauser, Zeitsch. anorg. Chem. LIII, 74; LIV, 196.

above). The chief soluble salts are the nitrate and the sulphate. The hydroxide of zirconium is insoluble in excess of the alkali hydroxides, the double sulphate with potassium is insoluble in a solution of potassium sulphate, and the oxalate is soluble in ammonium oxalate. Solutions of pure zirconium salts are said to give no precipitate with hydrofluoric acid or potassium hydronitride. Turmeric paper, when dipped into a solution of a zirconium salt and dried, is colored orange.

**Estimation.** Zirconium is usually weighed as the oxide ( $\text{ZrO}_2$ ) obtained by ignition of the hydroxide or oxalate.

**Separation.** Zirconium, with the other rare earths, may be roughly separated from other elements by the action of oxalic acid (*vid.* page 48.) For the separation from yttrium, cerium, and thorium see under those elements. The separation of zirconium from iron and titanium has received a good deal of attention from chemists. Some of the methods that have been suggested follow.

From iron zirconium may be separated (1) by the action of water upon an ethereal solution of the chlorides,—the oxychloride of zirconium being precipitated (Matthews, Jour. Amer. Chem. Soc. xx, 846); (2) by the action of gaseous hydrochloric acid and chlorine at a temperature of about  $200^\circ \text{C}$ . upon the mixed oxides,—the ferric chloride being volatilized (Havens and Way, Amer. Jour. Sci. [4] VIII, 217); (3) by treatment with phenylhydrazine,—the zirconium being precipitated (Allen, Jour. Amer. Chem. Soc. xxv, 426); (4) by the action of sulphurous acid on neutral solutions,—the zirconium being precipitated (Baskerville, Jour. Amer. Chem. Soc. xvi, 475).

From titanium zirconium may be separated (1) by boiling a solution containing the two elements with dilute sulphuric and acetic acids,—titanic acid being precipitated free from zirconium (Streit and Franz, J. pr. Chem. cviii, 75; Zeitsch. anal. Chem. ix, 388); (2) by treating solu-

tions acid with sulphuric or hydrochloric acid with zinc until the titanium is reduced to the condition of the sesquioxide, and then adding potassium sulphate,—the zirconium-potassium sulphate being precipitated (Pisani, *Compt. rend.* LVII, 298; *Chem. News* x, 91, 218); (3) by adding hydrogen dioxide and sodium phosphate to the solution,—the basic phosphate of zirconium being precipitated (Hillebrand, *Bull. U. S. Geol. Survey* No. 176, 75).

### EXPERIMENTAL WORK ON ZIRCONIUM.

*Experiment 1. Extraction of zirconium salts from zircon.* Fuse 5 grm. of finely powdered zircon in a platinum or nickel crucible with about 15 grm. of acid potassium fluoride. Pulverize the fused mass and extract with hot water containing a few drops of hydrofluoric acid.\* Filter immediately through a rubber funnel into a rubber beaker. As the filtrate cools, potassium fluozirconate crystallizes out. It may be purified by recrystallization.

*Experiment 2. Precipitation of zirconium hydroxide,  $(\text{Zr}(\text{OH})_4)$ .* (a) To a solution of a zirconium salt add potassium, sodium, or ammonium hydroxide. Note the insolubility in excess. (b) To a solution containing zirconium add sodium thiosulphate in solution and boil.

*Experiment 3. Precipitation of zirconium carbonate,  $(3\text{ZrO}_2 \cdot \text{CO}_2 + 8\text{H}_2\text{O})$ .* (a) To a solution of a zirconium salt add sodium or potassium carbonate. Note the partial solubility in excess.

(b) Use ammonium carbonate as the precipitant. Note the solvent action of an excess and the precipitation of the hydroxide on boiling.

(c) Try the action of the common acids upon separate portions of zirconium carbonate.

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\* Glass or porcelain dishes must not be used when hydrofluoric acid is present.

*Experiment 4. Precipitation of zirconium oxalate,  $(Zr(C_2O_4)_2 \cdot 2Zr(OH)_4)$ .* (a) To a solution of a zirconium salt add a solution of oxalic acid. Note the effect of an excess in the cold and on warming.

(b) Use ammonium oxalate as the precipitant. Note the solvent action of an excess and the reprecipitation by ammonium hydroxide.

*Experiment 5. Precipitation of zirconium phosphate,  $(xZrO_2 \cdot yP_2O_5, \text{basic})$ .* To a solution of a zirconium salt add sodium phosphate. Orthophosphoric acid precipitates the normal phosphate  $(Zr_3(PO_4)_4)$ .

*Experiment 6. Precipitation of zirconium ferrocyanide,  $(ZrFeC_6N_6?)$ .* To a solution of a zirconium salt add potassium ferrocyanide.

*Experiment 7. Action of zirconium salts upon turmeric paper.* Dip a piece of turmeric paper into a solution of a zirconium salt acidified with hydrochloric acid. Dry on the side of a test-tube or beaker, as in testing for boric acid. Note the yellowish-red color.

*Experiment 8. Negative tests of zirconium salts.* Note that neither hydrogen sulphide nor potassium fluoride gives a precipitate with zirconium salts. Ammonium sulphide precipitates the hydroxide, not the sulphide.



## CHAPTER V.

### GALLIUM,\* Ga, 69.9.

**Discovery.** In 1875 Lecoq de Boisbaudran, who had done much work with spectrum analysis, notified the Académie des Sciences of his discovery of a new element in a zinc-blende from the mine of Pierrefitte in the Pyrenees, and proposed for it the name Gallium (Compt. rend. LXXXI, 493; Chem. News xxxii, 159). The individuality of the new body was distinctly indicated by the spectroscope, but so small was the amount of it in the possession of the discoverer that few of its reactions were determined. Among the properties which he described, however, were the following: the oxide, or perhaps a subsalt, was thrown down by metallic zinc in a solution containing chlorides and sulphates; in a mixture containing an excess of zinc chloride the new body was the first to be precipitated by ammonia; in the presence of zinc it was concentrated in the first sulphides deposited; the spark spectrum of the concentrated chloride showed two violet lines, one of them of considerable brilliance.

**Occurrence.** Gallium is found combined, in very small amounts, in certain minerals, chiefly zinc-blendes from Bensberg on the Rhine, Pierrefitte, and other localities. It has been detected in some American zinc-blendes (Chem. Ztg. (1880), 443). The Bensberg sphalerite, one of the richest sources, contains 0.016 grm. per kilo.

Hartley and Ramage obtained the following interesting results by means of the spectroscope (Jour. London Chem.

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\* The discovery of gallium was predicted by Mendeléeff in 1869, and the hypothetical element was named Ekaluminum. It was given the atomic weight of 68, and the specific gravity of 6.

Soc. (1897), 533, 547): the presence of gallium was indicated in thirty-five out of ninety-one iron ores examined; in all the magnetites, seven in number; in all the aluminum ores, fifteen in number, mostly kaolin and bauxite; in four out of twelve manganese ores; and in twelve out of fourteen zinc-blendes.

**Extraction.** Salts of gallium are obtained by the following process: The mineral is dissolved in aqua regia and the excess of acid expelled by boiling. When the solution is cold, pure zinc is added, which precipitates the antimony, arsenic, bismuth, copper, cadmium, gold, lead, mercury, silver, tin, selenium, tellurium, and indium. These are filtered off while there is still some evolution of hydrogen, and the filtrate is boiled from six to twenty-four hours with metallic zinc. Gallium is precipitated as a basic salt, together with salts of aluminum, iron, zinc, etc. To obtain the gallium salt in a more nearly pure condition the precipitate is dissolved in hydrochloric acid, the solution is treated with hydrogen sulphide, and after filtration and the removal of the excess of hydrogen sulphide by boiling, sodium carbonate is added in small portions. The gallium salt is the first to be precipitated, and the precipitates are collected as long as they show the gallium lines in the spark spectrum.\* These precipitates are dissolved in sulphuric acid and the solution is diluted largely with water and boiled. The basic sulphate of gallium which is thus thrown down is dissolved in sulphuric acid, and potassium hydroxide is added in excess. Iron if present is removed at this point by filtration and the gallium oxide is then precipitated from the filtrate by carbon dioxide. The discoverer prepared 62 grams of the element from 2400 kilograms of blende.

**The Element.** *A. Preparation.* Gallium in the elementary condition has been obtained by subjecting an alkaline solution of the oxide to electrolysis.

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\* Two violet lines, 4171 and 4031.

**B. Properties.** A gray, lustrous metal, showing greenish-blue lights on reflecting surfaces, gallium is malleable and fairly hard. Its fusing point,  $30.15^{\circ}\text{C.}$ , is so low that it melts readily from the warmth of the hand. In water, and in air at ordinary temperatures, it is unchanged; when heated in air or oxygen it is oxidized only superficially. It combines rapidly with chlorine, more slowly with bromine, and not at all with iodine unless heat is applied. Gallium is soluble in hydrochloric and warm nitric acids, and somewhat soluble in potash and ammonia solutions. It alloys easily with aluminum, and these alloys decompose cold water rapidly. Its specific gravity is 6.

**Compounds.** *A. Typical forms.* The following compounds of gallium are known:

Oxides .....	$\text{GaO?}$	$\text{Ga}_2\text{O}_3$
Hydroxide .....		$\text{Ga}(\text{OH})_3?$
Chlorides .....	$\text{GaCl}_2$	$\text{GaCl}_3$
Bromide .....		$\text{GaBr}_3$
Iodide .....		$\text{GaI}_3$
Nitrate .....		$\text{Ga}_2(\text{NO}_3)_6$
Sulphate .....		$\text{Ga}_2(\text{SO}_4)_3$
Double sulphate .....		$\text{Ga}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 + 24\text{H}_2\text{O}$

**B. Characteristics.** The compounds of gallium resemble those of aluminum and indium in forming alums and in having a hydroxide soluble in excess of sodium or potassium hydroxide. The salts are colorless and soluble, and in dilute solutions tend, on being heated, to become basic and separate from the solution. The oxide ( $\text{Ga}_2\text{O}_3$ ) is insoluble in acids and alkalis after ignition.

**Estimation.** Gallium is usually weighed as the oxide ( $\text{Ga}_2\text{O}_3$ ).

**Separation.\*** *Vid.* Extraction.

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\* For a detailed study of the separation of gallium, see many articles by Lecoq de Boisbaudran, *Compt. rend.* xciv-xcviii.

**INDIUM, In, 114.8.)**

**Discovery.** Indium was discovered by Reich and Richter in 1863, in the course of an examination of two ores consisting mainly of the sulphides of arsenic, zinc, and lead (J. pr. Chem. LXXXIX, 441). These ores had been freed from the greater part of their arsenic and sulphur by roasting, and the residue had been evaporated to dryness with hydrochloric acid and distilled. The crude chloride of zinc thus obtained was examined with the spectroscope for thallium, since the presence of that element had been indicated in similar ores from the Freiberg mines. Instead of the thallium line, however, appeared one of indigo blue never before observed. The color suggested the name Indium for the unknown element present.

**Occurrence.** Indium occurs in very small amounts, combined with sulphur, in many zinc-blendes. It has been found in zinc-blende from Freiberg and Breitenbrunn in Saxony, and from Schönfeld in Bohemia; in christophite, a variety of zinc-blende; in zinc prepared from these ores; and in the flue-dust from ovens used for roasting zinc ores. It has also been found in wolframite from Zinnwald. The proportion of indium in the minerals named varies from one tenth of one per cent. to mere traces. Lockyer detected it in the atmosphere of the sun. Hartley and Ramage (Jour. London Chem. Soc. (1897), 533, 547) have discovered it spectroscopically in many iron ores,—notably siderites,—in some manganese ores, in zinc-blendes, in five tin ores examined, and in many pyrites.\*

**Extraction.** Indium salts may be obtained as follows from zinc that has been extracted from indium-bearing blendes. The crude metal is nearly dissolved in hydrochloric or nitric acid, and the solution is allowed to stand twenty-four hours with the undissolved metal. A spongy

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\* For further discussion of the wide distribution of this element *vid.* Wernadski, Bull. Acad. St. Petersburg (1911), 187 and 1007.

mass, consisting of the indium together with lead, copper, cadmium, tin, arsenic, and iron, collects upon the residual zinc. This mass is washed with water containing some sulphuric acid; it is then dissolved in nitric acid and evaporated with sulphuric acid until all the nitric acid is removed. By this process the lead is precipitated, and it may be removed by filtration. The solution that remains is treated with ammonium hydroxide in excess, and the hydroxides of iron and indium are filtered off and dissolved in a small amount of hydrochloric acid. This solution is treated with an excess of acid sodium sulphite and boiled. Indium is precipitated as the basic sulphite ( $\text{In}_2(\text{SO}_3)_3 \cdot \text{In}_2(\text{OH})_6 + 5\text{H}_2\text{O}$ ). Indium may also be separated from iron by treating the chlorides with potassium sulphocyanide and extracting the ferric sulphocyanide with ether. Again, it may be separated from aluminum and iron by treating the chlorides in alcoholic solution with pyridine. The indium is precipitated as a compound of indium chloride and pyridine ( $\text{InCl}_3 \cdot 3\text{C}_5\text{H}_5\text{N}$ ) (Dennis, Ber. Dtsch. chem. Ges. xxxvii, 961; Renz, *ibid.* xxxvii, 2110; Mathers, Jour. Amer. Chem. Soc. xxx, 209).

**The Element.** *A. Preparation.* Elementary indium may be obtained (1) by heating the oxide with carbon or in a current of hydrogen; (2) by heating the oxide with sodium under a layer of dry sodium chloride; (3) by treating the salts with zinc; (4) by electrolyzing the sulphate in the presence of formic acid (Dennis).

*B. Properties.* Indium is a soft white metal, less volatile than cadmium and zinc. It melts at  $155^\circ \text{C}$ . (Thiel). At ordinary temperatures it is stable in the air, but when heated it ignites and burns with a violet flame to the oxide. It does not decompose boiling water. It dissolves easily in hydrochloric, nitric, and sulphuric acids. It forms alloys with lead and thallium. Its specific gravity is given at from 7.1 to 7.4.

**Compounds.\*** *A. Typical forms.* The following compounds of indium are known:

Oxides .....	$\text{InO}; \text{In}_2\text{O}_3$
Hydroxide.....	$\text{In}(\text{OH})_3$
Fluoride.....	$\text{InF}_3 + 3\text{H}_2\text{O}$
Chlorides.....	$\text{InCl}; \text{InCl}_2; \text{InCl}_3$
Oxychloride. ....	$\text{InOCl}$
Indium - hydrochloric acid.....	$\text{H}_2\text{InCl}_4$
Bromide .....	$\text{InBr}_3$
Iodide.....	$\text{InI}_3$
Nitrate .....	$\text{In}_2(\text{NO}_3)_6 + 9\text{H}_2\text{O}$
Sulphate .....	$\text{In}_2(\text{SO}_4)_3$
Double sulphates....	$\text{In}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 + 24\text{H}_2\text{O};$ $\text{In}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 + 24\text{H}_2\text{O}$
Sulphite.....	$\text{In}_2(\text{SO}_3)_3 \cdot \text{In}_2(\text{OH})_6 + 5\text{H}_2\text{O}$
Sulphides.....	$\text{In}_2\text{S}; \text{InS}; \text{In}_2\text{S}_3$
Sulpho salts.....	$\text{K}_2\text{In}_2\text{S}_4; \text{Na}_2\text{In}_2\text{S}_4$

*B. Characteristics.* Indium resembles aluminum in forming alums with potassium and ammonium sulphates, and in having a hydroxide soluble in excess of potassium or sodium hydroxide. It resembles zinc in forming a sulphide with hydrogen sulphide, but in the case of indium this salt is yellow. Indium monoxide is a dark powder slowly soluble in dilute acids. The sesquioxide is a yellowish-white powder easily soluble in warm acid and more infusible than aluminum oxide. The dichloride is formed directly by the union of chlorine with the metal, and is a white, crystalline mass. In water it separates into the trichloride and the metal. By fusion of the dichloride with elementary indium the monochloride is formed,—a

\* The following references will be found helpful: Thiel, *Zeitsch. anorg. Chem.* XL, 280; LXVI, 288; Mathers, *Jour. Amer. Chem. Soc.* XXX, 485; XXX, 86, 211. J

reddish-black, crystalline substance. The trichloride is formed also by the action of chlorine in excess upon the metal; it is white like the dichloride and dissolves in water with the evolution of heat. The nitrate and the sulphate are readily soluble in water and tend to form basic salts on being heated. Solutions of indium salts color the flame violet and give a characteristic flame spectrum.

**Estimation.** Indium is generally determined as the oxide, ( $\text{In}_2\text{O}_3$ ), obtained by ignition of the hydroxide, or as the sulphide, ( $\text{In}_2\text{S}_3$ ), obtained by precipitation with hydrogen sulphide in the presence of sodium acetate.

**Separation.** The separation of this very rare element from those elements with which it is usually associated is treated under Extraction.

### THALLIUM, Tl, 204.

**Discovery.** Some years previous to 1861 Crookes had been engaged in the extraction of selenium from a seleniferous deposit which he had obtained from the sulphuric-acid manufactory at Tilkerode in the Hartz Mountains. Some residues, left after the purification of the selenium, and supposed to contain tellurium, were set aside and not examined until 1861, when, needing tellurium, Crookes vainly tried to isolate it by various chemical methods. At length he resorted to spectrum analysis and tested some of the residue in the flame. The spectrum of selenium appeared, and as it was fading, and he was looking for evidence of tellurium, a new bright-green line flashed into view. The element whose presence was thus indicated received the name Thallium, from the Greek *θαλλός*, or the Latin *thallus*, a budding twig (Chem. News III, 194).

About the same time Lamy announced the discovery of the same element (Ann. Chim. Phys. [3] LXVII, 385), but after much discussion and the presentation of much

evidence on both sides it was declared that Crookes had the priority of discovery.

**Occurrence.** Thallium occurs in certain very rare minerals:

*Crookesite*,  $(\text{Cu}, \text{Tl}, \text{Ag})_2\text{Se}$  contains 16–19% Tl

*Lorandite*,  $\text{TlAsS}_2$ , “ 59–60% Tl

*Hutchinsonite*,  $(\text{Tl}, \text{Ag}, \text{Cu})_2\text{S} \cdot \text{As}_2\text{S}_3 + \text{PbS} \cdot \text{As}_2\text{S}_3$ , contains 18–25% Tl

It is found also in very small quantities in berzelianite,  $(\text{Cu}_2\text{Se})$ ; in some zinc-blendes and copper pyrites; in iron pyrites from Theux, Namur, Philippeville, Alais, and Nantes; in lepidolite from Mähren; and in mica from Zinnwald. It has been detected, together with cæsium, rubidium, and potassium, in the mineral waters of Nauheim and Orb. Its presence in the flue-dust from some iron furnaces and sulphuric-acid works, as well as in some crude sulphuric and hydrochloric acids, may be traced to its presence in the pyrites used. It has been found in commercial platinum.

**Extraction.** Thallium salts may be extracted by the following methods:

(1) *From minerals.* The finely powdered mineral is dissolved in aqua regia. The solution is evaporated with sulphuric acid until the free acid has been removed; it is then diluted abundantly with water, neutralized with sodium carbonate, and treated with potassium cyanide in excess. This precipitates the bismuth and lead, which are filtered off. The filtrate is treated with hydrogen sulphide, which precipitates the cadmium, mercury, and thallium as the sulphides. Very dilute sulphuric acid dissolves the thallium sulphide, leaving the cadmium and mercury sulphides undissolved (Crookes).

(2) *From flue-dust.* The material is treated with an equal weight of boiling water in a large wooden tub, and is allowed to stand twenty-four hours. The liquid is si-



phoned off and is precipitated with hydrochloric acid.\* The crude chloride thus obtained is treated with an equal weight of sulphuric acid, and heated to expel the hydrochloric acid and the greater part of the excess of sulphuric. The sulphate obtained is dissolved in water, the solution is neutralized with chalk and filtered. By the addition of hydrochloric acid to the filtrate, nearly pure thallous chloride is precipitated (Chem. News VIII, 159).

**The Element.** *A. Preparation.* The element thallium may be obtained (1) by fusing a mixture of thallous chloride and sodium carbonate with potassium cyanide; (2) by submitting the carbonate or the sulphate to electrolysis; (3) by heating the oxalate; and (4) by precipitating with zinc from an alkaline solution of a thallous salt.

*B. Properties.* Metallic thallium is in color whitish to blue gray, with the luster of lead. It is soft and malleable and melts at  $285^{\circ}\text{C}$ . It forms alloys with many of the metals (Kurnakow, Zeitsch. anorg. Chem. xxx, 86; LII, 430; Baar, *ibid.* LXX, 352). It oxidizes readily at high temperatures, but is not acted upon by water free from air. It is soluble in dilute nitric and sulphuric acids. It is a poor conductor of electricity. The specific gravity of thallium is 11.88.

**Compounds.**† *A. Typical forms.* The following are typical compounds of thallium:

Oxides.....	$\text{Tl}_2\text{O}$	$\text{Tl}_2\text{O}_3$
Hydroxides.....	$\text{TlOH}$	$\text{Tl}(\text{OH})_3$
Carbonate.....	$\text{Tl}_2\text{CO}_3$	
Chlorides.....	$\text{TlCl}$	$\text{TlCl}_3 + \text{H}_2\text{O}$
Double chlorides..	$\text{TlCl} \cdot \text{HgCl}_2$ ; $3\text{TlCl} \cdot \text{FeCl}_3$ ; $\text{TlCl} \cdot \text{AuCl}_3$ ; etc.	$\text{TlCl}_3 \cdot 3\text{KCl} + 2\text{H}_2\text{O}$ ; etc.
Chlorate.....	$\text{TlClO}_3$	
Perchlorate.....	$\text{TlClO}_4$	

\* Three tons of dust gave sixty-eight pounds of crude thallous chloride.

† See also Hawley, Jour. Amer. Chem. Soc. xxix, 300, 1011; Stortenbeker, Rec. trav. chim. Pays-Bas, xxvi, 248; Thomas, Ann. chim. phys. xi [8], 204.

Bromides .....	TlBr	TlBr <sub>3</sub>
Double bromides..		TlBr <sub>3</sub> ·KBr + 2H <sub>2</sub> O; TlBr <sub>3</sub> ·3TlBr
Bromate.....	TlBrO <sub>3</sub>	
Iodides .....	TlI	TlI <sub>3</sub>
Double iodides....	TlI·KI	TlI <sub>3</sub> ·NH <sub>4</sub> I
Iodates .....	TlIO <sub>3</sub>	Tl(IO <sub>3</sub> ) <sub>3</sub>
Periodate .....		3Tl <sub>2</sub> O <sub>3</sub> ·I <sub>2</sub> O <sub>7</sub> + 30H <sub>2</sub> O
Thiosulphate.....	Tl <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	
Sulphides .....	Tl <sub>2</sub> S	Tl <sub>2</sub> S <sub>3</sub>
Sulphite .....	Tl <sub>2</sub> SO <sub>3</sub>	
Sulphates .....	Tl <sub>2</sub> SO <sub>4</sub> ; TlHSO <sub>4</sub>	Tl <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
Double sulphates..	with MgSO <sub>4</sub> , ZnSO <sub>4</sub> , CuSO <sub>4</sub> , etc.	
Alums.....	Tl <sub>2</sub> SO <sub>4</sub> ·Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 24H <sub>2</sub> O; Tl <sub>2</sub> SO <sub>4</sub> ·Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 24H <sub>2</sub> O	
Nitrates.....	TlNO <sub>3</sub>	Tl(NO <sub>3</sub> ) <sub>3</sub> + 4H <sub>2</sub> O
Phosphates.....	Tl <sub>3</sub> PO <sub>4</sub> ; Tl <sub>4</sub> P <sub>2</sub> O <sub>7</sub> ; TlPO <sub>3</sub>	TlPO <sub>4</sub> + 2H <sub>2</sub> O
Arseniates.....	Tl <sub>3</sub> AsO <sub>4</sub>	TlAsO <sub>4</sub> + 2H <sub>2</sub> O
Cyanides.....	TlCN	Tl(CN) <sub>3</sub> ·TlCN
Sulphocyanide....	TlSCN	
Ferrocyanide .....	Tl <sub>4</sub> Fe(CN) <sub>6</sub> + 2H <sub>2</sub> O	
Silicofluoride .....	Tl <sub>3</sub> SiF <sub>6</sub>	
Chromates.....	Tl <sub>2</sub> CrO <sub>4</sub> ; Tl <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	
Chloroplatinate ...	Tl <sub>2</sub> PtCl <sub>6</sub>	
Molybdate.....	Tl <sub>2</sub> MoO <sub>4</sub>	
Tungstate .....	Tl <sub>2</sub> WO <sub>4</sub>	
Vanadates.....	Tl <sub>3</sub> VO <sub>4</sub> ; Tl <sub>4</sub> V <sub>2</sub> O <sub>7</sub> ; TlVO <sub>3</sub>	

*B. Characteristics.* Thallium compounds are known in two conditions of oxidation, the thallos, (Tl<sub>2</sub>O), and the thallic, (Tl<sub>2</sub>O<sub>3</sub>). The lower condition is the more stable; consequently the thallos compounds are the more numerous and the better known. When the metal is allowed to oxidize in the air it forms the thallos oxide, but when it is melted in an atmosphere of oxygen, thallic oxide is obtained. Thallic chloride, bromide, and iodide may be formed by treating the corresponding thallos salts with an excess of chlorine, bromine, and iodine, respectively. In general, the thallos salts may be oxidized to the thallic form by strong oxidizing agents, such as potassium permanganate, lead dioxide, barium dioxide, etc. Thallium in the lower condition resembles the alkalis potassium,

cæsium, and rubidium in having a soluble hydroxide, carbonate, and sulphate, and an insoluble chloroplatinate and cobaltic nitrite; also in forming alums. It resembles lead in forming an insoluble sulphide and chromate, and in having halogen salts difficultly soluble in cold water but readily soluble in hot water. The thalious salts are colorless when the base is combined with a colorless acid. The sulphide is brownish black. The thallic salts are in general unstable, and on being heated with water tend to precipitate the oxide ( $Tl_2O_3 \cdot H_2O$ ). They may be easily reduced to the lower condition by the action of reducing agents. They may be formed by the careful treatment of thallic oxide with acids as well as by the action of strong oxidizing agents upon the thalious salts. Thallic hydroxide is insoluble, and resembles ferric hydroxide in color. The halogen salts, the nitrate and the sulphate of thallium in the thallic condition are soluble. Solutions of thallium salts in either condition of oxidation give to the flame a characteristic green color.

**Estimation.\*** *A. Gravimetric.* Thallium is generally weighed in the thalious condition (1) as the chloroplatinate, ( $Tl_2PtCl_6$ ), after precipitation by chloroplatinic acid (Crookes, *Select Methods*, Second Edition, 380); (2) as the iodide (TII), after precipitation by potassium iodide (Werther, *Zeitsch. anal. Chem.* III, 1, and J. B. (1864), 712; Long, *Zeitsch. anal. Chem.* xxx, 342); (3) as the chromate ( $Tl_2CrO_4$ ), after precipitation in alkaline solution by potassium chromate (Browning and Hutchins, *Amer. Jour. Sci.* [4] VIII, 460); (4) as the sulphate ( $Tl_2SO_4$ ), after evaporation of appropriate salts with sulphuric acid in ex-

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\* See also Heberling, *Liebig Annal.* cxxxv, 207; Phipson, *Compt. rend.* xxviii, 563; Neumann, *Liebig Annal.* ccxlv, 349; Feit, *Zeitsch. anal. Chem.* xxviii, 314; Carnot, *Compt. rend.* cix, 177; Sponholz, *Zeitsch. anal. Chem.* xxxi, 519; Thomas, *Compt. rend.* cxxx, 1316; Marshall, *Jour. Soc. Chem. Ind.* xix, 994.

cess and ignition at low red heat, or as the acid sulphate, ( $\text{TiHSO}_4$ ), obtained by substituting for ignition heating at  $220^\circ\text{--}240^\circ\text{C}$ . (Browning, Amer. Jour. Sci. [4] IX, 137). It may be estimated also by weighing the gold precipitated according to the equation:  $3\text{TiCl} + 2\text{AuBr}_3 = 2\text{Au} + 3\text{TiClBr}_2$  (Thomas, Ann. chim. phys. XI [8], 204).

*B. Volumetric.* Thallium is estimated volumetrically (1) by the oxidation of thallous salts with permanganate (Crookes, Select Methods, Second Edition, 381); (2) by the action of potassium iodide upon thallic salts, as shown in the following equation (Thomas, Compt. rend. CXXXIV, 655):  $\text{TiCl}_3 + 3\text{KI} = \text{TiI} + 3\text{KCl}_2 + \text{I}_2$ .

**Separation.\*** In the more stable thallous condition, to which thallic salts may readily be reduced, thallium may be separated as follows: from the metals which give precipitates with hydrogen sulphide in acid (but not acetic) solution, by hydrogen sulphide; from elements which form insoluble hydroxides with the alkali hydroxides, by these reagents; and from the alkalies and alkali earths, by ammonium sulphide.

## EXPERIMENTAL WORK ON THALLIUM.

*Experiment 1. Extraction of thallium salts from fluo-dust.* The method described under Extraction may be followed.

*Experiment 2. Precipitation of thallous chloride, bromide, and iodide ( $\text{TiCl}$ ;  $\text{TiBr}$ ;  $\text{TiI}$ ).* (a) To a solution of a thallous salt add hydrochloric acid or a chloride in solution. Note the solvent action of boiling water. Try the effect of cooling the hot solution.

(b) Repeat the experiment, using potassium bromide as the precipitant.

(c) Try similarly potassium iodide.

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\* See Crookes, Select Methods, Second Edition, 382-386.

*Experiment 3. Precipitation of thallium chloroplatinate* ( $\text{Tl}_2\text{PtCl}_6$ ). To a solution of a thallous salt add a few drops of a solution of chloroplatinic acid.

*Experiment 4. Precipitation of thallium cobaltic nitrite.* To a solution of a thallous salt add a few drops of a solution of sodium cobaltic nitrite.

*Experiment 5. Precipitation of thallous chromate* ( $\text{Tl}_2\text{CrO}_4$ ). To a solution of a thallous salt add some potassium chromate in solution. Try the action of acids upon the precipitate.

*Experiment 6. Precipitation of thallous sulphide* ( $\text{Tl}_2\text{S}$ ). (a) Through a solution of a thallous salt acidified with dilute sulphuric acid pass hydrogen sulphide. Note the absence of precipitation. Divide the solution, and to one part add ammonium acetate and to the other ammonium hydroxide.

(b) Try the action of ammonium sulphide upon a thallous salt in solution.

*Experiment 7. Oxidation of thallous salts.* (a) To a solution of a thallous salt acidified with sulphuric acid add gradually a little potassium permanganate. Note the disappearance of the color of the permanganate.

(b) To a solution of a thallous salt add bromine water until the color of the bromine ceases to fade. To one portion add a few drops of a solution of a chloride or bromide. Note the absence of precipitation. To another portion add sodium or potassium hydroxide. Note the precipitation of brown thallic hydroxide, ( $\text{Tl}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ).

*Experiment 8. Reduction of a thallic salt.* To a solution of a thallic salt formed, for example, as in Experiment 7 (b) add stannous chloride. Note the precipitation of thallous chloride, ( $\text{TlCl}$ ).

*Experiment 9. Flame and spectroscopic tests for thal-*

*lium salts.* (a) Dip the end of a platinum wire into a solution of a thallium salt and hold it in the flame of a Bunsen burner. Note the green color.

(b) Examine spectroscopically the flame colored by a solution of a thallium salt. Observe the green line.

*Experiment 10. Negative tests of thallous salts.* Note that sulphuric acid and the alkali hydroxides and carbonates give no precipitate with solutions of thallous salts.

## CHAPTER VI.

### TITANIUM, Ti, 48.1.

**Discovery.** In the year 1791 McGregor (Crell Annal. (1791) I, 40, 103) discovered a new "metal" in a magnetic sand found in Menachan, Cornwall. This sand he named Menachinite, and the newly discovered element Menachite. Four years later Klaproth announced the discovery of a new earth in a rutile which he was engaged in studying (Klapr. Beitr. I, 233). To the metal of this earth he gave the name Titanium, in allusion to the Titans. In 1797, however, he found that titanium was identical with menachite (Klapr. Beitr. II, 236).

**Occurrence.** Titanium is found combined in many minerals, but never in considerable quantity in any one locality.

	Contains $\text{TiO}_2$
<i>Rutile</i> , $\text{TiO}_2$ .....	90-100%
<i>Dicksbergite</i> , <i>vid.</i> <i>Rutile</i> .....	90-100%
<i>Brookite</i> , $\text{TiO}_2$ .....	90-100%
<i>Octahedrite</i> , $\text{TiO}_2$ .....	90-100%
<i>Pseudobrookite</i> , $\text{Fe}_4(\text{TiO}_4)_3$ .....	44- 53%
<i>Perovskite</i> , $\text{CaTiO}_3$ .....	58- 59%
<i>Ilmenite</i> , $\text{FeTiO}_3$ .....	3- 59%
<i>Magnetite</i> , $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ .....	0- 6%
<i>Bauxite</i> , $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ .....	0-4.5%
<i>Geikielite</i> , $\text{MgO} \cdot \text{TiO}_2$ .....	67- 68%
<i>Senaite</i> , $(\text{Fe,Pb})\text{O} \cdot 2(\text{Ti,Mn})\text{O}_2$ .....	57- 58%

Zirkelite, $(\text{Ca}, \text{Fe})\text{O} \cdot 2(\text{Zr}, \text{Ti}, \text{Th})\text{O}_2$ .....	14— 15%
Knopite, $\text{RO} \cdot \text{TiO}_2$ .....	54— 59%
Derbylite, $6\text{FeO} \cdot 5\text{TiO}_2 \cdot \text{Sb}_2\text{O}_5$ .....	34— 35%
Lewisite, $5\text{CaO} \cdot 2\text{TiO}_2 \cdot 3\text{Sb}_2\text{O}_5$ .....	11— 12%
Mauzeliite, $4(\text{Ca}, \text{Pb})\text{O} \cdot \text{TiO}_2 \cdot 2\text{Sb}_2\text{O}_5$ .....	7— 8%
Titanite, $\text{CaTiSiO}_5$ .....	34— 42%
Neptunite, $\overset{\text{I}}{\text{R}}_2\overset{\text{II}}{\text{R}}\text{TiSi}_4\text{O}_{12}$ .....	17— 18%
Keilhauite, complex silicate.....	26— 36%
Schlormenite, $3\text{CaO}(\text{Fe}, \text{Ti})_2\text{O}_3 \cdot 3(\text{Si}, \text{Ti})\text{O}_2$ .....	12— 22%
Guarinite, $\text{CaTiSiO}_5$ .....	33— 34%
Tscheffkinit, complex silicates.....	16— 21%
Astrophyllite, $(\text{Na}, \text{K})_4(\text{Fe}, \text{Mn})_4\text{Ti}(\text{SiO}_4)_4$ .....	7— 14%
Leucosphenite, $\text{Na}_4\text{Ba}(\text{TiO})_2(\text{Si}_2\text{O}_5)_5$ .....	13— 14%
Johnstrupite, complex silicates.....	7— 8%
Mosandrite, “ “.....	5— 10%
Rhönite, “ “.....	9— 10%
Rinkite, “ “.....	13— 14%
Narsarsukite, “ “.....	14%
Benitoite, $\text{BaTiSi}_3\text{O}_9$ .....	20%
Lorenzenite, $\text{Na}_2(\text{TiO})_2\text{Si}_2\text{O}_7$ .....	35%
Delorenzite, complex.....	66%
Dysanalyte, $6(\text{Ca}, \text{Fe})\text{TiO}_3 \cdot (\text{Ca}, \text{Fe})\text{Nb}_4\text{O}_6$ .....	40— 59%
Pyrochlore, $\text{RNb}_2\text{O}_6 \cdot \text{R}(\text{Ti}, \text{Th})\text{O}_3$ .....	5— 14%
Æschynite, $\overset{\text{III}}{\text{R}}_2\text{Nb}_4\text{O}_{18} \cdot \overset{\text{III}}{\text{R}}_2(\text{Ti}, \text{Th})_6\text{O}_{18}$ .....	21— 22%
Polymignite, $5\text{RTiO}_3 \cdot 5\text{RZrO}_3 \cdot \text{R}(\text{Nb}, \text{Ta})_2\text{O}_6$ .....	18— 19%
Yttrocrasite, complex titanite.....	49— 50%
Marignacite, <i>vid.</i> Pyrochlore.....	2— 3%
Euxenite, $\overset{\text{III}}{\text{R}}(\text{NbO}_3)_3 \cdot \overset{\text{III}}{\text{R}}_2(\text{TiO}_3)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ .....	20— 23%
Polycrase, $\overset{\text{III}}{\text{R}}(\text{NbO}_3)_3 \cdot 2\overset{\text{III}}{\text{R}}(\text{TiO}_3)_3 \cdot 3\text{H}_2\text{O}$ .....	25— 29%
Blomstrandite, complex.....	10— 19%
Yttrotitanite <i>vid.</i> Keilhauite.	

Titanium has been found also in sand on the banks of the North Sea, in some mineral waters, in certain varieties of



coal, in meteorites, and by means of the spectroscope it has been detected in the atmosphere of the sun. It has been found in the ash of oak, apple, and pear wood, in cow peas, in cotton-seed meal, and in the bones of men and animals. *Vid.* also Baskerville, Jour. Amer. Chem. Soc. XXI, 1099.

**Extraction.** Titanium salts may be extracted from rutile by the following methods:

(1) The mineral is fused with three parts of a mixture of sodium and potassium carbonates and the fused mass is extracted with water. The titanium, as a sodium or potassium titanate, remains, together with some tin and iron, in the insoluble residue. This mass is treated with strong hydrochloric acid until dissolved. The solution is then diluted, and the tin is removed by hydrogen sulphide. The sulphide of tin is filtered off, the filtrate is made ammoniacal with ammonium hydroxide and again treated with hydrogen sulphide. The iron is precipitated as the sulphide, and the titanium as the hydroxide. After filtration the precipitate is suspended in water and a current of sulphur dioxide is passed through until the black sulphide of iron has dissolved, leaving the oxide of titanium.

(2) The mineral is fused with three parts of acid potassium fluoride and the fused mass is extracted with hot water and a little hydrofluoric acid. The titanium separates, on cooling, as the potassium fluotitanate ( $K_2TiF_6 + H_2O$ ).

(3) The mineral, finely pulverized, is fused with three times its weight of sodium dioxide and the melt is extracted with water. The titanium remains in solution (H. D. Newton).

(4) The mineral is fused with six parts of acid potassium sulphate (*vid.* Experiment 1).

(5) The mineral is mixed with carbon and heated in the electric furnace. The carbide thus formed is converted into the chloride by heating it with dry chlorine (Stähler, Ber. Dtsch. chem. Ges. XXXVIII, 2619).

(6) The mineral is heated to  $1000^{\circ}$  and chilled in water. The powder is mixed with aluminum (one-half its weight) and ignited by burning magnesium. On heating the metal obtained to a red heat in a current of dry chlorine titanium tetrachloride distils (Ellis, Chem. News, xcv, 122).

**The Element.** *A. Preparation.* Elementary titanium may be obtained (1) by heating potassium fluotitanate with potassium (Berzelius and Wöhler); (2) by heating the chloride ( $\text{TiCl}_4$ ) in a bomb with metallic sodium (Hunter, Jour. Amer. Chem. Soc. xxxii, 330). *Vid.* also Weiss, Zeitsch. anorg. Chem. lxxv, 345.

*B. Properties.* As prepared by Hunter, titanium resembles polished steel. It is quite brittle when cold and readily malleable at low red heat. It does not decompose water at ordinary temperatures and acts on heated water but slightly. When heated in the air it combines with the oxygen, burning brightly to the oxide ( $\text{TiO}_2$ ); in oxygen the combination is accompanied with brilliant light. Titanium is readily soluble in warm hydrochloric acid, and is attacked by dilute hydrofluoric, nitric, sulphuric, and acetic acids. It combines with chlorine. It combines also with nitrogen, forming nitrides. It melts between  $1800^{\circ}$  and  $1850^{\circ}$  and its specific gravity is 4.5.

**Compounds.** *A. Typical forms.* The following are typical compounds of titanium:

Oxides . . .	$\text{TiO}$ ; $(\text{Ti}_3\text{O}_4)$ ; $\text{Ti}_2\text{O}_3$ ; $(\text{Ti}_7\text{O}_{12})$ ; $\text{TiO}_2$ ; $(\text{Ti}_2\text{O}_5)$ ; $\text{TiO}_3$	
Hydroxides		$\text{Ti}(\text{OH})_4^*$ $\text{Ti}(\text{OH})_6$
Chlorides . .	$\text{TiCl}_3$	$\text{TiCl}_4$
Bromide . . .		$\text{TiBr}_4$
Iodide . . . .		$\text{TiI}_4$
Fluoride . . .		$\text{TiF}_4$
Titanofluorides . . . .		$\text{R}_2\text{TiF}_6$ , etc.
Sulphides . .	$\text{Ti}_2\text{S}_3$	$\text{TiS}_2$

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\* Orthotitanic acid.

Sulphates ..	$\text{Ti}_2(\text{SO}_4)_3$	$\text{Ti}(\text{SO}_4)_2$
Nitrides ...		$\text{Ti}_3\text{N}_4$ ; $\text{Ti}_5\text{N}_6$ ; $\text{TiN}_2$
Carbide ...		$\text{TiC}$
Silicide. . . .		$\text{TiSi}$
Titanates (meta)		$\text{RTiO}_3$ ; $\text{R}_2\text{TiO}_3$
Acids ( <i>vid.</i> Hydroxides) ...		$\text{H}_2\text{TiO}_3$

*B. Characteristics.* Although a number of oxides of titanium are known, the dioxide is the form generally found, and the salts of that type are by far the most numerous and important. The oxide ( $\text{TiO}_2$ ) resembles the oxide of zirconium ( $\text{ZrO}_2$ ) in acting as a weak base. It forms salts with the strong acids, but does not combine with the weak acids. It unites with the strong bases to form titanates, ( $\text{RTiO}_3$  and  $\text{R}_2\text{TiO}_3$ ). It has less basic and more acidic properties than the oxide of zirconium. The tetrachloride is a colorless liquid which fumes in the air. Practically all the salts of titanium are insoluble in water, the presence of free acid being necessary to prevent the formation of insoluble basic compounds. Titanium, in its behavior toward reagents, resembles quite closely both niobium and tantalum, with which it is often found associated (*vid.* Occurrence).

**Estimation.\*** *A. Gravimetric.* Titanium is usually precipitated as the acid, either by ammonium hydroxide or by boiling a dilute solution acidified with acetic or sulphuric acid; the precipitate is ignited and the element is determined as the oxide ( $\text{TiO}_2$ ).

*B. Volumetric.* Titanium is estimated volumetrically (1) by treating with hydrogen dioxide a definite amount of the titanium solution to be determined and comparing its color with that of a definite amount of a standard solution of titanium similarly treated (Weller,

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\* For estimation in ores see Technical Methods of Ore Analysis, Low, John Wiley & Sons, New York, 1906.

Ber. Dtsch. chem. Ges. xv, 2592); (2) by reducing the titanium from the dioxide to the sesquioxide condition, by the use of zinc and hydrochloric acid, and then oxidizing it with permanganate (Osborn, Amer. Jour. Sci. [3] xxx, 329); (3) by reducing the titanium from the dioxide to the sesquioxide condition in an atmosphere of hydrogen, by means of zinc and sulphuric acid, then oxidizing it by an excess of ferric salt, and estimating the titanium originally present by titrating with potassium permanganate the ferrous salt formed (Newton, Amer. Jour. Sci. xxv (1908), 130).

**Separation.** The general method for the separation of titanium from the other members of the aluminum group is to boil dilute acidified solutions (*vid.* Gravimetric Estimation). The titanium precipitate, however, carries down traces of other elements, as aluminum and iron.

From iron titanium may be separated (1) by passing hydrogen sulphide into an alkaline solution to which ammonium tartrate has been added,—the iron sulphide being precipitated (Gooch, Amer. Chem. Jour. vii, 283); (2) by treating a mixture of ferrous sulphide and titanous acid with sulphur dioxide (*vid.* Extraction); (3) by boiling a neutral solution with hydrogen dioxide,—metatitanous acid being precipitated; (4) by shaking a solution of the chlorides with ether, the ferric chloride dissolving.

From aluminum titanium may be separated by boiling a solution containing them, in the presence of an alkali acetate and of acetic acid to about seven per cent. of the whole solution,—titanium basic acetate being precipitated (Gooch, Amer. Chem. Jour. vii, 283).

From cerium and thorium titanium may be separated by precipitating the double sulphates of those elements with potassium sulphate. Methods for the separation from zirconium have already been given (*vid.* Zirconium). From niobium and tantalum titanium may be separated\* by

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\* E. F. Smith, Proc. Amer. Philos. Soc. XLIV (1905), 151, 177.

repeated fusions with acid potassium sulphate and extractions of the melt with water,—the titanium being in soluble form. A satisfactory separation of niobium from titanium may be effected by crystallizing the niobium-potassium oxyfluoride from 35% hydrofluoric acid. The titanium remains in solution (C. W. Balke and E. F. Smith, Jour. Amer. Chem. Soc. xxx, 1637).

### EXPERIMENTAL WORK ON TITANIUM.

#### *Experiment 1. Extraction of titanium salts from rutile.*

(a) Mix 5 grm. of finely powdered mineral with about 30 grm. of acid potassium sulphate and fuse until the mass is free from black particles. Pulverize the fused mass and extract with cold water, stirring frequently until solution is complete. Add ammonium sulphide, filter and wash. Suspend the precipitate, which consists mainly of titanium hydroxide and ferrous sulphide, in water and pass a current of sulphur dioxide through the liquid until the ferrous sulphide has dissolved, as shown by the disappearance of the dark color. Filter, and wash the titanium hydroxide which remains.

(b) *Alternative method.* After having dissolved the fused mass in cold water (*vid. (a)*) add about 20 grm. of tartaric acid and make the solution faintly ammoniacal. Pass hydrogen sulphide until the iron is completely precipitated. Filter, add about 10 cm.<sup>3</sup> of concentrated sulphuric acid to the filtrate, and evaporate in a porcelain dish under a draught hood until the tartaric acid is thoroughly carbonized. Allow the mass to stand until cool, add water, keeping the liquid cool to prevent the precipitation of the titanium hydroxide, and decant from the carbon residue. Filter the brown liquid through animal charcoal previously freed from phosphates, and precipitate the titanium hydroxide with ammonium hydroxide (R. G. Van Name). The tartaric acid may be decomposed by fuming nitric acid and the

titanium quantitatively determined. (W. M. Thornton, Amer. Jour. Sci. xxxiv, 214).

*Experiment 2. Precipitation of titanium hydroxide,  $(\text{Ti}(\text{OH})_4)$ .* (a) To a solution containing titanium add sodium, potassium, or ammonium hydroxide. Note the comparative insolubility in excess, especially in ammonium hydroxide. Repeat, having hydrogen dioxide present in the solution.

(b) Repeat the experiment, using the alkali carbonates. The precipitate is the same as in (a).

(c) Note the solubility of the freshly precipitated hydroxide in the common acids.

(d) Ignite a portion of the precipitate and try its solubility in acids.

*Experiment 3. Precipitation of titanic hydroxide or acid by boiling.* (a) Boil a dilute acid solution of titanic hydroxide. Note the precipitation. Filter, and test the filtrate with ammonium hydroxide.

(b) To a solution of titanic acid containing enough free acid to prevent precipitation on boiling, add ammonium acetate. Try similarly sodium thiosulphate.

*Experiment 4. Precipitation of basic titanic phosphate,  $(\text{Ti}(\text{OH})\text{PO}_4)$ .* To a solution containing titanic acid add a little sodium phosphate in solution. Repeat, having hydrogen dioxide present in the solution.

*Experiment 5. Color tests of solutions containing titanium.* (a) To an acid solution containing titanium add hydrogen dioxide. Note the yellow color ( $\text{TiO}_3$  in solution).

(b) To a solution containing titanium add a piece of metallic zinc and enough acid to start the action. Note the violet color which develops.

*Experiment 6. Negative test of titanium compounds.* Pass hydrogen sulphide through a solution containing titanium. Note the absence of precipitation.

**GERMANIUM,\*** Ge, 72.5.

**Discovery.** In 1886 Clemens Winkler announced the presence of a new element in the silver mineral argyrodite, which had been discovered the previous year by Weisbach, in the Himmelsfürst mine near Freiberg (Ber. Dtsch. chem. Ges. XIX, 210). According to Winkler's analysis of argyrodite, the sum of its component parts was seven per cent. less than it should have been; and although he repeated the analysis several times with great care, the outcome was always the same. This uniformity of result forced upon him the conclusion that an unknown element was probably present; and after much careful and patient work he was successful in isolating it and investigating its properties. On heating the mineral out of contact with the air, he obtained a dark-brown fusible sublimate, which proved to be chiefly two sulphides, that of the new element, named by him Germanium, and the sulphide of mercury.

**Occurrence.** Germanium is found in combination in a few rare minerals.

	Contains Ge
<i>Argyrodite</i> , $4\text{Ag}_2\text{S} \cdot \text{GeS}_2$ . . . . .	6-7%
<i>Canfieldite</i> , $4\text{Ag}_2\text{S} \cdot (\text{Ge}, \text{Sn})\text{S}_2$ . . . . .	1.82%
<i>Euxenite</i> , $\overset{\text{III}}{\text{R}}(\text{NbO}_3)_3 \cdot \overset{\text{III}}{\text{R}}_2(\text{TiO}_3)_3 \cdot \frac{3}{2}\text{H}_2\text{O}$ . . . . .	traces

It occurs also in some zinc-blendes.

**Extraction.** Germanium salts have been extracted as follows:

(1) A Hessian crucible is heated to redness, and small quantities of a mixture consisting of three parts of sodium

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\* The discovery of this element was predicted by Mendeléeff in 1869 and the hypothetical element was named Ekasilicon. It was given an atomic weight of 72, and a specific gravity of 5.5. Its oxide, chloride, ethide, and fluoride, as described by Mendeléeff, resemble closely the corresponding compounds of Ge.

carbonate, six parts of potassium nitrate, and five parts of argyrodite are gradually put in. After being heated for some time the molten mass is poured into an iron dish and allowed to cool. The salt mass may then be removed from the silver, pulverized, and extracted with water. The extract is treated with sulphuric acid and evaporated until all the nitric acid is driven off. The residue is dissolved in water and allowed to stand until the oxide of germanium separates from the solution.

(2) Treat the finely powdered zinc-blende with strong sulphuric acid, and evaporate to dryness. Dissolve in water and add sodium sulphide. Treat the sulphide with sulphuric acid (15 : 100). The sulphide of germanium remains, and the sulphide of zinc dissolves (Urbain, *Compt. rend. cl.*, 1758).

**The Element.** *A. Preparation.* Elementary germanium may be obtained (1) by heating the oxide with carbon; (2) by heating the oxide in a current of hydrogen.

*B. Properties.* Germanium is a grayish-white, metallic element, having a fine luster, and crystallizing in regular octahedra. It volatilizes slightly when heated in hydrogen or nitrogen at about  $1350^{\circ}$  C.; its melting-point is about  $900^{\circ}$  C. In the air it does not oxidize at ordinary temperatures, but when heated goes over to the oxide  $\text{GeO}_2$ . It is not attacked by dilute hydrochloric acid, is oxidized by nitric acid, and is dissolved by aqua regia. It is dissolved also by sulphuric acid, with the evolution of sulphur dioxide. It combines directly with chlorine, bromine, and iodine. Its specific gravity is 5.46.

**Compounds.** *A. Typical forms.* The following are typical compounds of germanium:

Oxides.....	$\text{GeO}$	$\text{GeO}_2$
Chlorides.....	$\text{GeCl}_2$	$\text{GeCl}_4$
Oxychloride.....		$\text{GeOCl}_2$
Bromide.....		$\text{GeBr}_4$



Iodide.....	$\text{GeI}_4$
Fluoride.....	$\text{GeF}_4$ ; $\text{K}_2\text{GeF}_6$ ; $\text{H}_2\text{GeF}_6$
Sulphides. ....	$\text{GeS}_2$
Chloroform. ....	$\text{GeHCl}_3$
Ethyl.....	$\text{Ge}(\text{C}_2\text{H}_5)_4$

*B. Characteristics.* The germanium compounds are known in two conditions of oxidation; those of the higher form are the more stable and comprise the larger group. Germanium resembles carbon and silicon in the formation of a chloroform, and tin in the formation of two sulphides which dissolve in ammonium sulphide, giving sulpho salts. The sulphide  $\text{GeS}_2$  is a white powder slightly soluble in water. The lower sulphide,  $\text{GeS}$ , when precipitated, is of a reddish-brown color; when obtained by the reduction of the higher sulphide it is a grayish-black crystalline substance of metallic luster. This sulphide, also, is slightly soluble in water. The dioxide is a white powder soluble in alkalis, but almost completely insoluble in acids. The tetrachloride is a liquid which fumes in damp air and is decomposed by water. Germanium compounds give a characteristic spark spectrum in the blue and violet.

**Estimation.** Germanium is usually precipitated as the sulphide, converted by nitric acid into the oxide ( $\text{GeO}_2$ ), and weighed as such.

**Separation.** Germanium may be separated from most of the elements by the formation of a soluble sulpho salt with ammonium sulphide; when the solution is acidified the sulphide is precipitated. Germanium may be separated from arsenic, antimony, and tin as follows: the solution of the sulpho salts is exactly neutralized with sulphuric acid, allowed to stand twelve hours, and filtered; the filtrate is evaporated to a small volume, treated with ammonia and sulphate of ammonium, acidified with sulphuric acid, and saturated with hydrogen sulphide. Germanium sulphide is precipitated (Truchot, *Les Terres Rares*, 294).

## CHAPTER VII.

### VANADIUM, V, 51.

**Discovery.** As early as 1801 Del Rio announced the discovery of a new metal in a lead ore from Zimapan, Mexico. He named it Erythronium (*ἐρυθρός*, *red*), because its salts became red when heated with acids (Annal. der Phys. u. Chem. LXXI, 7). Four years later Collet Descotils examined the supposed metal and pronounced it an impure oxide of chromium,—a conclusion that Del Rio himself came to accept (Ann. de Chim. LIII, 268).

In 1830 Sefström found an unknown metal in an iron ore from Taberg, Sweden. He proposed for it the name Vanadium, from Vanadis, the Scandinavian goddess more commonly known as Freya (Amer. Jour. Sci. [1] xx, 386). Almost immediately Wöhler showed the identity of vanadium with the metal described by Del Rio (Pogg. Annal. XXI, 49).

**Occurrence.** Vanadium is found quite widely distributed, always in combination, and in very small quantities:

	Contains V <sub>2</sub> O <sub>5</sub> .
<i>Vanadinite</i> , (PbCl)Pb <sub>4</sub> (VO <sub>4</sub> ) <sub>3</sub> .....	8-21%
<i>Descloizite</i> , (Pb,Zn) <sub>2</sub> (OH)VO <sub>4</sub> .....	20-22%
<i>Eusynchite</i> , <i>vid.</i> <i>Descloizite</i> .....	17-24%
<i>Dechenite</i> , <i>vid.</i> <i>Descloizite</i> .....	45-47%
<i>Cuprodescloizite</i> , (Pb,Zn,Cu) <sub>2</sub> (OH)VO <sub>4</sub> .....	17-22%
<i>Calciovolborthite</i> , (Cu,Ca) <sub>2</sub> (OH)VO <sub>4</sub> .....	37-39%
<i>Carnotite</i> ,* K <sub>2</sub> O·2UO <sub>2</sub> ·V <sub>2</sub> O <sub>5</sub> ·3H <sub>2</sub> O (doubtful)....	19-20%

\* Amer. Jour. Sci. x, 138.

	Contains $V_2O_5$ .
Brackebuschite, formula doubtful.....	24-25%
Psittacinite, formula doubtful.....	17-26%
Volborthite, " " .....	14-15%
Pucherite, $BiVO_4$ .....	22-27%
Roscoelite, silicate, formula doubtful.....	21-29%
Ardennite, " " " .....	traces-9%
Mottramite, $(Cu,Pb)_5V_2O_{10} \cdot 2H_2O$ .....	17-18%
Chileite, <i>vid.</i> Mottramite.....	13-14%
Vanadiolite, silico-calcium vanadate .....	44-45%
Vanadic ocher .....	100%
Bismuth ocher, formula doubtful .....	1-29%
Patronite, * $VS_4 + nS$ .....	18-19% V.

Vanadium has been detected also in some copper, lead, and iron ores, in certain clays and basalts, in soda ash and phosphate of soda, and in some hard coals.

**Extraction.** Vanadium salts may be extracted from mineral sources by the following methods.

(1) The mineral is fused with potassium nitrate, and the potassium vanadate thus formed is extracted with water. By the addition of a soluble lead or barium salt to the solution the lead or barium vanadate is precipitated. This insoluble vanadate is decomposed by means of sulphuric acid, and the barium or lead sulphate is filtered off. By saturation of the filtrate with ammonium chloride the ammonium vanadate is precipitated.

(2) Finely ground carnotite is decomposed by nitric acid, and the solution is treated with sodium hydroxide and sodium carbonate; the vanadium is left in soluble form as sodium vanadate. If vanadinite is used instead of carnotite the lead must be precipitated from the nitric acid solution by hydrogen sulphide, and the excess of hydrogen sulphide removed from the filtrate by boiling, before the treatment with sodium hydroxide.

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\* Hillebrand, Jour. Amer. Chem. Soc. XXIX, 1019.

(3) The mineral, e. g., carnotite, is fused with acid potassium sulphate, the melt extracted with water, and the solution evaporated, when the double sulphates of vanadium and uranium with potassium crystallize out. The vanadium is reduced by zinc, and precipitated by ammonium hydroxide and ammonium carbonate.

(4) A patented process by J. H. Haynes (Mineral Resources U. S., 1906, page 531) for treatment of carnotite is of interest. The powdered mineral, previously roasted, is agitated with boiling sodium carbonate, which extracts vanadium and uranium. From this solution the uranium is precipitated by sodium hydroxide.

**The Element.** *A. Preparation.* Elementary vanadium may be prepared (1) by the action of "mischmetal" (metals of Ce and Y groups) on the oxide ( $V_2O_5$ ) (Muthmann and Weiss, *Liebigs Ann.*, cccxxxvii, 370; ccclv, 58); (2) by the action of aluminum or carbon on the trioxide (Ruff and Martin, *Zeitsch. angew. Chem.* xxv, 49).

*B. Properties.* Vanadium is a non-magnetic, light-gray powder, somewhat crystalline in appearance. It oxidizes slowly in the air at ordinary temperatures, but more rapidly when heated, going through various degrees of oxidation and showing a characteristic color for each oxide,—brown ( $V_2O$ ), gray ( $V_2O_2$ ), black ( $V_2O_3$ ), blue ( $V_2O_4$ ), and red ( $V_2O_5$ ). Upon the application of heat vanadium unites with chlorine, forming the chloride  $VCl_4$ ; at a red heat it combines with nitrogen, giving the nitride VN. It is insoluble in hydrochloric and dilute sulphuric acids, and soluble in nitric, hydrofluoric, and concentrated sulphuric acids. It is not attacked by alkaline solutions, but with melted alkalis forms the alkali vanadates, with the evolution of hydrogen. The specific gravity of vanadium is 5.68. The melting-point of the metal is  $1715^\circ \text{C}$ .

**Compounds.\*** *A. Typical forms.* The following may be considered typical compounds of vanadium:

Oxides.....	$V_2O$	$V_2O_3$	$V_2O_3^\dagger$	$V_2O_4$	$V_2O_5$
Chlorides.....		$VCl_3$	$VCl_4$	$VCl_4$	
Oxychlorides....			$VOCl$	$VOCl_2$	
Bromide.....			$VBr_3$		
Oxybromides....				$VOBr_2$	$VOBr_3$
Fluorides.....			$VF_3 + 6H_2O$		$VF_5$
Double fluorides..			$VF_3$ with $KF$ , $CoF_2$ , $NiF_2$ , etc.		
Sulphides.....	$V_2S_3$	$V_2S_3$			$V_2S_3O_2$ $V_2S_5$ $Na_2VS_3O$ $(NH_4)_3VS_4$ , etc. $V_2O_5(SO_4)_3$ $VN$ $\overset{I}{R}_3VO_4$ $\overset{I}{R}_4V_2O_7$ $\overset{I}{R}VO_5$ complex, $V_2O_5$ with $P_2O_5$ , $MoO_3$ , $WO_3$ , $SiO_2$ , $AsO_5$ , etc.
Sulpho salts.....					
Sulphate.....	$VSO_4$	$V_2(SO_4)_3$	$K_2SO_4 + 24H_2O$		
Nitrides.....		$VN$			
Vanadates, ortho,					
pyro,					
meta,					

*B. Characteristics.* The vanadium compounds are known in five conditions of oxidation, represented by the five oxides. Of these conditions the highest is the most stable and is known in the largest number of salts, the vanadates. Vanadic pentoxide is reddish yellow in color, and, like phosphoric pentoxide, it dissolves readily in the alkali hydroxides and carbonates. The alkali vanadates thus formed are of the ortho, pyro, and meta types,  $(\overset{I}{R}_3VO_4; \overset{I}{RV}_2O_7; \overset{I}{R}VO_5)$ . The vanadates are generally pale yellow in color. They are soluble in the stronger acids and with the exception of the alkali vanadates insoluble in water. Vanadic acid is easily reduced by reducing agents to the tetroxide condition, when the solution becomes blue. More powerful reducing agents carry the reduction further, to

\* See also *Das Vanadin und seine Verbindungen*, Ephraim, pub. by Ferdinand Enke, Stuttgart, 1904; Rütter, *Zeitsch. anorg. Chem.* **LII**, 368; Prandtl, *Ber. Dtsch. chem. Ges.* **XL**, 2125; Koppel, *Zeitsch. Electrochem.* **x**, 141.

† Dutton (*Jour. Amer. Med. Asso.*, June 3, 1911) describes a new form of poisoning called Vanadiumism caused by exposure to the fumes of vanadium trioxide.

the trioxide, or even the dioxide condition, but only long-continued heating in a current of hydrogen brings about the reduction to the monoxide and the element.

Hydrogen sulphide, acting upon vanadic acid, reduces it to the tetroxide condition or even below, with a separation of sulphur. Ammonium sulphide gives the dark-brown solution of a sulpho salt,  $((\text{NH}_4)_3\text{S}_2\text{VO}?)$ , and this solution, when acidified, gives a brown oxysulphide  $(\text{V}_2\text{S}_3\text{O}_2)$ . Vanadium resembles arsenic, phosphorus, and nitrogen, both in the chemical structure of its compounds and in their behavior toward reagents.

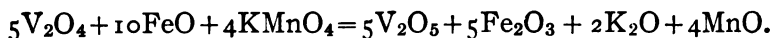
**Estimation.\*** *A. Gravimetric.* Vanadium is usually weighed as the pentoxide,  $(\text{V}_2\text{O}_5)$ , obtained (1) by precipitation of lead or barium vanadate, treatment with sulphuric acid, filtration, evaporation of the filtrate, and ignition; (2) by precipitation of mercury vanadate and ignition, the pentoxide being left; or (3) by precipitation of the ammonium salt by ammonium chloride and ignition (Berzelius, Pogg. Annal. xxii, 54; Gibbs, Amer. Chem. Jour. v, 371; Gooch and Gilbert, Amer. Jour. Sci. [4] xiv, 205).

*B. Volumetric.* Vanadium may be estimated volumetrically (1) by reduction from the condition of the pentoxide to that of the tetroxide by sulphur dioxide, hydrogen sulphide, or zinc and free acid, and reoxidation by permanganate (Hillebrand, Jour. Amer. Chem. Soc. xx, 461; Gooch and Gilbert, Amer. Jour. Sci. [4] xv, 389); (2) by effecting the reduction by boiling with hydrochloric acid or with potassium bromide or iodide in acid solution, according to the typical equation  $\text{V}_2\text{O}_5 + 2\text{HCl} = \text{V}_2\text{O}_4 + \text{H}_2\text{O} + \text{Cl}_2$ . The chlorine, bromine, or iodine may be dis-

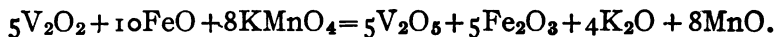
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\* See Die analytische Chemie des Vanadins, V. von Klecki, pub. by Leopold Voss, Hamburg, 1894; Campagne, Ber. Dtsch. chem. Ges. xxxvi, 3164; Beard, Ann. Chim. anal. et appl. x, 41; Chem. Zentr. 1905 [1], 960. For estimation in ores, see also Low's Technical Methods of Ore Analysis; Blair, Jour. Amer. Chem. Soc. xxx, 1229; Campbell, *ibid.* xxx, 1233.

tilled and determined by suitable means in the distillate (Holverschreit, Dissertation, Berlin, 1890; Friedheim, Ber. Dtsch. chem. Ges. xxviii, 2067; Gibbs, Proc. Amer. Acad. x, 250; Gooch and Stookey, Amer. Jour. Sci. [4] xiv, 369; Gooch and Curtis, Amer. Jour. Sci. [4] xvii, 4), or the residue after boiling may be rendered alkaline by potassium bicarbonate, and reoxidation effected by standard iodine solution (Browning, Amer. Jour. Sci. [4] ii, 185); (3) or the reduction may be accomplished by boiling with tartaric, oxalic, or citric acid, and reoxidation effected as outlined above (Browning, Zeitsch. anorg. Chem. vii, 158, and Amer. Jour. Sci. [4] ii, 355). (4) Vanadium and molybdenum may be estimated when together by heating their acids in the presence of sulphuric acid and treating with sulphur dioxide, which reduces the vanadium to the condition of the tetroxide, without affecting the molybdic acid. The vanadium may be estimated as in (1) by permanganate. The oxidized solution may then be passed through a Jones reductor into a receiver charged with a ferric salt. This process reduces the molybdenum to the sesquioxide ( $\text{Mo}_2\text{O}_3$ ) condition and the vanadium to the dioxide ( $\text{V}_2\text{O}_2$ ) condition, and registers the reduction in the ferric salt. The reoxidation is again effected with permanganate and the amount of vanadium being known from the first titration the molybdenum may be calculated from the second (Edgar, Amer. Jour. Sci. xxv (1908), 332). (5) By a similar process of differential reduction and oxidation Edgar (Amer. Jour. Sci. xxvi (1908), 79) estimates iron and vanadium in the presence of each other. After the solution containing vanadic acid and iron has been reduced by sulphur dioxide the oxidation by permanganate proceeds according to the equation:



After the reduction by zinc in the Jones reductor the oxidation is as follows:



From these equations, the amount of permanganate used being known, the amount of iron and vanadium present may be calculated.

**Separation.** Vanadium may be separated from the majority of the metallic bases (1) by fusion of material containing it with sodium carbonate and potassium nitrate and extraction with water, vanadium dissolving as sodium vanadate; or (2) by treatment of a solution containing a vanadate with ammonium sulphide in excess, vanadium remaining in solution as a sulpho salt.

From arsenic vanadium may be separated (1) by treatment with hydrogen sulphide, after reduction by means of sulphur dioxide, the arsenic being precipitated as the sulphide  $\text{As}_2\text{S}_3$ ; (2) by heating the sulphides of vanadium and arsenic in a current of hydrochloric-acid gas at  $150^\circ\text{C}$ ., the arsenic forming a volatile compound (Field and Smith, Jour. Amer. Chem. Soc. xviii, 1051).

From phosphorus vanadium may be separated by reduction of vanadic acid by means of sulphur dioxide, and precipitation of the phosphorus as phosphomolybdate.

From molybdenum the separation may be accomplished by the action of hydrogen sulphide upon a solution of vanadic and molybdic acids under pressure,—molybdenum sulphide being precipitated,—or by the action of ammonium chloride in excess upon a solution containing an alkali vanadate and molybdate,—ammonium metavanadate being precipitated (Gibbs, Amer. Chem. Jour. v, 371).

From tungsten vanadium may be separated by the ammonium chloride method (*vid.* Separation from molybdenum, above) (Gibbs, Amer. Chem. Jour. v, 379).



## EXPERIMENTAL WORK ON VANADIUM.

*Experiment 1. Extraction of vanadium from carnotite.* Treat 20 grm. of the finely powdered mineral with hydrochloric acid, heat until nothing further dissolves, dilute, pass hydrogen sulphide, and filter. Evaporate the filtrate nearly to dryness, add enough nitric acid to oxidize the vanadium to vanadic acid. To the oxidized solution add sodium hydroxide in excess, warm, and filter. The filtrate should contain sodium vanadate together with an excess of sodium hydroxide. Neutralize carefully with acetic acid and test for vanadium by any of the following experiments:

*Experiment 2. Formation of insoluble vanadates of lead, silver, barium and ammonium,  $(\overset{\text{II}}{\text{R}}_3(\text{VO}_4)_2$ , ortho; or  $\overset{\text{II}}{\text{R}}(\text{VO}_3)_2$ , meta).*

To separate portions of a solution of an alkali vanadate (ortho or meta) add (a) a solution of lead acetate; (b) silver nitrate; (c) barium chloride; (d) ammonium chloride (in solid form). Try the action of nitric and acetic acids upon the precipitated salts.

*Experiment 3. Formation of vanadium pentoxide,  $(\text{V}_2\text{O}_5)$ , from ammonium vanadate.* Evaporate a solution of ammonium vanadate to dryness and ignite. Note the crystals of the pentoxide.

*Experiment 4. Precipitation of vanadium oxysulphide,  $(\text{V}_2\text{S}_3\text{O}_2)$ .* (a) To a solution of an alkali vanadate add ammonium sulphide. Note the darkening in color ( $(\text{NH}_4)_3\text{S}_3\text{VO?}$ ). Acidify the solution with hydrochloric acid. Note the precipitation of the oxysulphide.

(b) Note that hydrogen sulphide in an acid solution precipitates sulphur and leaves a blue solution ( $\text{V}_2\text{O}_4$ ).

(c) Pass hydrogen sulphide into a solution of a vanadate made strongly alkaline with ammonium hydroxide. Note the red color.

*Experiment 5. Reduction of vanadic acid,  $(\text{V}_2\text{O}_5)$ .* (a) To a solution of an alkali vanadate add a crystal of

tartaric acid and boil. Note the yellow-red color of the vanadic acid when the tartaric acid is first added, and the change to blue ( $V_2O_4$ ) produced on boiling.

(b) Neutralize the blue solution obtained in (a) with sodium or potassium bicarbonate, and add a solution of iodine in potassium iodide until, after the liquid has stood for a few moments, the color of the iodine remains. Bleach the excess of iodine with an alkaline solution of arsenious oxide. Note that the blue color has disappeared and the vanadium is in the condition of the pentoxide ( $V_2O_5$ ).

(c) Try the action of other reducing agents upon vanadic acid, e.g. oxalic acid, hydrochloric acid, stannous chloride, zinc and hydrochloric acid, etc. Note that the zinc and hydrochloric acid carry the reduction below the tetroxide condition ( $V_2O_4$ ) \*

*Experiment 6. Delicate tests for vanadium. Formation of pervanadic acid, ( $HVO_4$ ).* (a) Acidify a solution of an alkali vanadate and add hydrogen dioxide. Note the red color (Maillard).

(b) Bring a few drops of the vanadium solution into contact with a drop of strong sulphuric acid to which a crystal of strychnine sulphate has been added. Note the color, changing from violet to rose.

*Experiment 7. Borax-bead tests for vanadium.* Fuse a little ammonium vanadate into a borax bead and test the action of the reducing and oxidizing flames upon it.

### NIOBIUM (COLUMBIUM), Nb(Cb), 93.5;

### TANTALUM, Ta, 181.5.

**Discovery.** Hatchett, while working with some chromium minerals in the British Museum in 1801, came across a black mineral very similar to those upon which he was engaged (Phil. Trans. Roy. Soc. (1802), 49). He obtained

\* The following series of colors obtained by the action of a reducing agent upon vanadic acid is given by Roscoe: yellow ( $V_2O_5$ ), green ( $V_2O_5 + V_2O_4$ ), bluish-green ( $V_2O_5 + V_2O_4$ ), blue ( $V_2O_4$ ), greenish-blue ( $V_2O_4 + V_2O_5$ ), green ( $V_2O_3 + V_2O_5$ ), bluish-violet ( $V_2O_3 + V_2O_5$ ), lavender or violet ( $V_2O_3$ ).

permission to examine it and found it to consist almost wholly of iron and an earth which did not conform to any known test. He described it as "a white, tasteless earth, insoluble in hot and cold water, acid to litmus, infusible before the blowpipe, and not dissolved by borax." The only acid which dissolved it was sulphuric. Since the mineral was of American origin, coming from Connecticut, the discoverer named it Columbite, and the element Columbium.

About a year later Ekeberg (*Crell Annal.* (1803) 1, 3), while investigating a mineral from Kimito, Finland, which closely resembled columbite, discovered a "metal" which resembled tin, tungsten, and titanium. It proved to be none of these, but in fact a new element. He named it Tantalum, "because even when in the midst of acid it was unable to take the liquid to itself." Indeed, insolubility in acid seemed to be the chief characteristic of the new substance.

The apparent similarity of columbium and tantalum suggested that they might be identical, and in order to settle this question Wollaston (*Phil. Trans. Roy. Soc.* xcix, 246) in 1809 began to work on tantalite and a specimen of the same columbite that Hatchett had examined. He found that the freshly precipitated acids were both soluble in concentrated mineral acids; if they were dried it was necessary to fuse them both with caustic alkalies before they could be dissolved. Both were held up if ammonium hydroxide was added in the presence of citric, tartaric, or oxalic acid. Having found practically the same reactions with both acids, he concluded that the elementary substances were the same. The specific gravity of tantalite, however, was 7.95, and that of columbite 5.91. This he explained by suggesting different conditions of oxidation or different states of molecular structure. These conclusions were accepted, and for many years the element was called indifferently tantalum and columbium.

In 1844 Rose began to investigate the same subject. His work on the columbites of Bodenmais and Finland led him to the belief that there were two distinct acids in the columbite from Bodenmais, one similar to that in tantalite, the other containing a new element, to which he gave the name Niobium, from Niobe, daughter of Tantalus. Though niobium proved to be Hatchett's columbium, Rose's name for the element has been the one more generally adopted, although the name columbium is now growing in favor.

**Occurrence.\*** Niobium and tantalum are found, each in combination, in various rare minerals. They usually, though not invariably, occur together.

	Contains	
	Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>
<i>Pyrochlore</i> , RNb <sub>2</sub> O <sub>6</sub> · R(Ti,Th)O <sub>3</sub> .....	47-58%	
<i>Chalcolamprite</i> , <i>vid.</i> <i>Pyrochlore</i> .....	59-60%	
<i>Marignacite</i> , <i>vid.</i> <i>Pyrochlore</i> .....	55-56%	5- 6%
<i>Koppite</i> , R <sub>2</sub> Nb <sub>2</sub> O <sub>7</sub> · $\frac{2}{3}$ NaF .....	61-62%	
<i>Hatchettolite</i> , 2R(Nb,Ta) <sub>2</sub> O <sub>6</sub> · R <sub>2</sub> (Nb,Ta) <sub>2</sub> O <sub>7</sub> .....	63-67%†	
<i>Microlite</i> , Ca <sub>2</sub> Ta <sub>2</sub> O <sub>7</sub> .....	7- 8%	68-69%
<i>Fergusonite</i> , (Y,Er,Ce)(Nb,Ta)O <sub>4</sub> .....	14-46%	4-43%
<i>Blomstrandine-Priorite</i> , complex .....	18-37%	0-1%
<i>Sipylite</i> , R <sup>III</sup> NbO <sub>4</sub> .....	47-48%	1- 2%
<i>Columbite</i> , (Fe,Mn)(Nb,Ta) <sub>2</sub> O <sub>6</sub> .....	26-77%	1-77%
<i>Tantalite</i> , FeTa <sub>2</sub> O <sub>6</sub> .....	3-40%	42-84%
<i>Neotantalite</i> , <i>vid.</i> <i>Tantalite</i> .....	23%	60-61%
<i>Skogbölite</i> , FeTa <sub>2</sub> O <sub>6</sub> .....	3-40%	42-84%
<i>Tapiolite</i> , Fe(Nb,Ta) <sub>2</sub> O <sub>6</sub> .....	11-12%	73-74%
<i>Mossite</i> , Fe(Nb,Ta) <sub>2</sub> O <sub>6</sub> .....	83%†	
<i>Yttrotantalite</i> , R <sup>III</sup> R <sup>III</sup> <sub>2</sub> (Ta,Nb) <sub>4</sub> O <sub>15</sub> .....	12-13%	46-47%
<i>Samarskite</i> , R <sup>III</sup> <sub>2</sub> R <sup>III</sup> <sub>3</sub> (Nb,Ta) <sub>6</sub> O <sub>21</sub> .....	41-56%	14-27%
<i>Nohlite</i> , <i>vid.</i> <i>Samarskite</i> .....	50-51%	
<i>Loranskite</i> , complex .....		47%

\* See also Schilling, *Zeitsch. angew. Chem.* (1905), 883.

† Nb<sub>2</sub>O<sub>5</sub> + Ta<sub>2</sub>O<sub>5</sub>.

	Contains	
	Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>
Stibiotantalite, Sb <sub>2</sub> O <sub>3</sub> (Ta,Nb) <sub>2</sub> O <sub>5</sub> ? . . . . .	7.5 %	51 %
Ännerödite, complex . . . . .	48-49 %	
Hielmite, complex . . . . .	4-16 %	55-72 %
Æschynite, $\overset{\text{III}}{\text{R}}_2\text{Nb}_4\text{O}_{13} \cdot \overset{\text{III}}{\text{R}}_2(\text{Ti,Th})_5\text{O}_{13}$ . . . . .	32-33 %	21-22 %
Polymignite, 5RTiO <sub>3</sub> · 5RZrO <sub>3</sub> · R(Nb,Ta) <sub>2</sub> O <sub>6</sub> . . . . .	11-12 %	1- 2 %
Euxenite, $\overset{\text{III}}{\text{R}}(\text{NbO}_3)_3 \cdot \overset{\text{III}}{\text{R}}_2(\text{TiO}_3)_3 \cdot \frac{3}{2}\text{H}_2\text{O}$ . . . . .	18-35 %	
Polycrase, $\overset{\text{III}}{\text{R}}(\text{NbO}_3)_3 \cdot 2\overset{\text{III}}{\text{R}}_2(\text{TiO}_3)_3 \cdot 3\text{H}_2\text{O}$ . . . . .	19-25 %	0- 4 %
Wöhlerite, $12\text{R}(\text{Si,Zr})\text{O}_3 \cdot \text{RNb}_2\text{O}_6$ . . . . .	12-14 %	
Låvenite, $\text{R}(\text{Si,Zr})\text{O}_3 \cdot \text{Zr}(\text{SiO}_3)_2 \cdot \text{RTa}_2\text{O}_6$ . . . . .	0- 5 %*	
Dysanallyte, $6\text{RTiO}_3 \cdot \text{RNb}_2\text{O}_6$ . . . . .	0-23 %	0- 5 %
Kochelite, <i>vid.</i> Fergusonite . . . . .	29-30 %	
Arrhenite, complex . . . . .	2- 3 %	21-22 %
Blomstrandite, complex . . . . .	49-50 %*	
Rogersite, . . . . .	18-20 %	
Adelpholite, <i>vid.</i> Sipylite . . . . .	41-42 %*	
Vietingshofite, <i>vid.</i> Samarskite . . . . .	51 %*	
Eucolite, complex silicates . . . . .	2- 4 %*	
Melanocerite, complex silicates . . . . .		3- 4 %
Caryocerite, <i>vid.</i> Melanocerite . . . . .		3.1 %
Steenstrupine, <i>vid.</i> Melanocerite . . . . .	0-1.5 %*	
Cyrtolite, silicate . . . . .	0-1.5 %*	
Naegite, silicate . . . . .	4 %	7 %
Tritomite, complex silicates . . . . .		1- 3 %
Cassiterite (Ainalite), SnO <sub>2</sub> . . . . .		0- 9 %

**Extraction.** Salts of niobium and tantalum may be extracted from columbite or tantalite by either of the following methods:

(1) The mineral is fused with six parts of potassium bisulphate, the fused mass is pulverized and treated with hot water and dilute hydrochloric acid. The residue is

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\* Nb<sub>2</sub>O<sub>5</sub> + Ta<sub>2</sub>O<sub>5</sub>.

then digested with ammonium sulphide to remove tin, tungsten, etc., and again warmed with dilute hydrochloric acid. After this treatment it is washed thoroughly with water and dissolved in hydrofluoric acid. Filtration is followed by the addition of potassium carbonate to the clear solution until a precipitate begins to form. The potassium and tantalum double fluoride separates first in needle-like crystals, after which the niobium oxyfluoride crystallizes in plates.

(2) The mineral is fused with three parts of acid potassium fluoride (*vid.* Experiment 1).

**The Elements.** I. NIOBIUM. *A. Preparation.* The element niobium may be obtained (1) by reducing the oxide with aluminum (Goldschmidt reaction); (2) by mixing the pentoxide with paraffin, drawing into fibers, and reducing to the tetroxide by heating with carbon. The tetroxide, being a conductor, is reduced to the metal by heating highly *in vacuo* (von Bolton, *Zeitsch. Electrochem.* XIII, 145); (3) by heating the oxide with "mischmetal" (Muthmann and Weiss, *Liebig Ann.* CCCXXXVII, 370; CCCLV, 58).

*B. Properties.* Niobium is a metallic element of steel-gray color and brilliant luster. Heated in the air it is only slowly oxidized to  $\text{Nb}_2\text{O}_4$ . It is practically unattacked by acids, except by a mixture of nitric and hydrofluoric acids, but is attacked by fused alkalis and at red heat by chlorine. It combines with hydrogen and nitrogen. It is as hard as wrought iron, and is malleable and ductile. Its fusing-point is  $1950^\circ \text{C.}$ , and its specific gravity is about 7.

II. TANTALUM.\* *A. Preparation.* Elementary tantalum may be obtained (1) by heating the potassium and tantalum fluoride ( $\text{K}_2\text{TaF}_7$ ) with potassium and extracting the potassium fluoride with water; (2) by heating the oxide with "mischmetal."

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\* Von Bolton, *Zeitsch. angew. Chem.* (1906), 1537; Muthmann, *Liebig Ann.* CCCLV, 58.

*B. Properties.* Tantalum in the elementary condition is a little darker in color than platinum, and is about as hard as soft steel. It can be hammered into plates and drawn into wire. In the cold it is very inert. Heated to  $400^{\circ}$  C. it becomes yellow, and to  $600^{\circ}$  bluish. At low redness it burns to the oxide. Its melting-point is given as  $2850^{\circ}$  C. (von Pirani) and  $2900^{\circ}$  C. (Waidner).<sup>\*</sup> It combines at low redness with hydrogen, nitrogen, and chlorine. It combines readily with carbon, forming several carbides. The metal is not attacked by hydrochloric, nitric, or sulphuric acid, but is attacked by hydrofluoric acid and by fused alkalis. The specific gravity of melted and drawn tantalum is 16.8; that of the metal in powder form (hydrogen and oxygen being present), 14.

*Compounds.*<sup>†</sup> *A. Typical forms.* The following are typical compounds of niobium and tantalum:

Oxides.....	Nb <sub>2</sub> O <sub>5</sub>	
	Nb <sub>2</sub> O <sub>4</sub>	Ta <sub>2</sub> O <sub>5</sub>
	Nb <sub>2</sub> O <sub>3</sub>	Ta <sub>2</sub> O <sub>3</sub>
Chlorides.....		(Ta <sub>6</sub> Cl <sub>12</sub> )Cl <sub>2</sub> ·7H <sub>2</sub> O ‡
	NbCl <sub>5</sub>	
	NbCl <sub>3</sub>	TaCl <sub>5</sub>
Oxychloride.....	NbOCl <sub>3</sub>	
Bromides.....	NbBr <sub>5</sub>	TaBr <sub>5</sub>
Oxybromide. ....	NbOBr <sub>3</sub>	
Fluorides.....	NbF <sub>5</sub>	TaF <sub>5</sub>
Oxyfluoride. ....	NbOF <sub>3</sub>	

<sup>\*</sup> Waidner and Burgess, *J. physique* vi, 380; *Chem. Abs.*, *Amer. Chem. Soc.* II, 739 (Mar. '08); von Pirani and Meyer, *Zeitsch. f. Electrochem.* xvii, 908.

<sup>†</sup> See also E. F. Smith and others, *Jour. Amer. Chem. Soc.* xxvii, 1140, 1216, 1369; xxx, 1637; xxxii, 323, 729; Chabrie, *Compt. rend.* cxliv, 804; Ruff and Schiller, *Zeitsch. anorg. Chem.* lxii, 329.

<sup>‡</sup> Chapin (*Jour. Amer. Chem. Soc.* xxxii, 323) has also prepared a corresponding bromide and iodide.

Fluotantalates ..	$K_2TaF_7$ $Na_2TaF_7$ $(NH_4)_2TaF_7$
Double fluorides.	$xKF \cdot yNbOF_3$ $xKF \cdot yNbO_2F$ } (typical)
Sulphide.....	$Nb_2OS_3$ $Ta_2S_4$
Silicide.....	$TaSi_2$
Nitride.....	$Ta_3N_8$
Niobates.....	$K_8Nb_6O_{19} + 16H_2O$ $K_6Nb_4O_{13} + 13H_2O$ $2K_2Nb_4O_{11} + 11H_2O$ $K_4Nb_2O_7 + 11H_2O$ $Na_{16}Nb_{14}O_{43}$ $Na_2Nb_2O_6$ , etc.
Tantalates *....	Of types $R_8Ta_6O_{19}$ and $RTaO_5$ , with Na, K, $NH_4$ , Ba, and Mg.

*B. Characteristics.* The compounds of niobium closely resemble those of tantalum, both in chemical form and in behavior toward reagents. The two elements are closely associated in minerals (*vid.* Occurrence). The lower oxides of niobium are dark powders which oxidize when heated. The dioxide is soluble in hydrochloric acid, while the tetroxide is not attacked by acids. The pentoxide is a yellowish-white amorphous powder somewhat soluble in concentrated sulphuric acid before ignition, but insoluble after. Niobium pentachloride is a yellow crystalline substance prepared by passing sulphur chloride ( $S_2Cl_2$ ) in the form of vapor over the pentoxide. It tends to form the oxychloride in the presence of water. It is reduced to the trichloride when its vapor is passed through a red-hot tube. The fluoride is formed by the action of hydrofluoric acid upon the pentoxide.

Tantalum tetroxide is a very hard, dark-gray, porous mass which is not attacked by acids. When heated it

\* *Vid.* also Wedekind and Maass, *Zeitsch. angew. Chem.* XXXIII, 2314.



goes over to the higher oxide. The pentoxide of tantalum is a white powder which is somewhat soluble in acids. The chloride and fluoride of tantalum are formed similarly to the corresponding salts of niobium and resemble them in general behavior. Niobates and tantalates are obtained by fusing the oxides with caustic alkalies; these salts are soluble. The tantalum compounds give no color test with morphia, tannic acid, or pyrogallic acid.

**Estimation.** *A. Gravimetric.* Niobium and tantalum are ordinarily weighed as the oxides  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$ , obtained from ignition of the acids.

*B. Volumetric.* Niobium may be estimated volumetrically by reduction from the condition of the pentoxide to that of the trioxide by means of zinc and hydrochloric acid in a current of carbon dioxide, and oxidation with permanganate (Osborn, Amer. Jour. Sci. [3] xxx, 329).

**Separation.** The method usually employed for the separation of niobium and tantalum from the elements with which they are generally associated—namely, titanium, zirconium, and thorium—is that of fusion with acid potassium sulphate (*vid.* Titanium). From tin and tungsten they may be separated by repeated fusions of the oxides with sodium carbonate and sulphur (E. F. Smith, Proc. Amer. Philos. Soc. XLIV, 157).

The separation of niobium from tantalum is one of the most difficult of analytical problems. Marignac's method (Ann. Chim. Phys. [4] VIII, 1) is based upon the difference in solubility\* between the tantalum-potassium fluoride ( $\text{K}_2\text{TaF}_7$ ) and the niobium-potassium oxyfluoride ( $2\text{KF} \cdot \text{NbOF}_3 + \text{H}_2\text{O}$ ). Foote and Langley (Amer. Jour. Sci. [4] xxx, 393) have devised an indirect method depending upon the difference in density ( $\text{Ta}_2\text{O}_5$ , 8.716 and  $\text{Nb}_2\text{O}_5$ , 4.552) of the oxides. They use as standards for comparison densities of mixtures of known content.

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\*  $\text{K}_2\text{TaF}_7$  is soluble in 151-157 parts of cold water.  $2\text{KF} \cdot \text{NbOF}_3 + \text{H}_2\text{O}$  is soluble in 12-13 parts of cold water.

## EXPERIMENTAL WORK ON NIOBIUM AND TANTALUM.

*Experiment 1. Extraction of niobium and tantalum salts from columbite or tantalite.* Mix 5 grm. of the finely ground mineral with 15 grm. of acid potassium fluoride and fuse thoroughly. Pulverize the fused mass and extract with boiling water containing a little hydrofluoric acid. Evaporate to about 200 cm.<sup>3</sup> and allow the liquid to stand. The potassium and tantalum fluoride separates first in needle-like form; the niobium and potassium oxyfluoride crystallizes in plates on concentration of the solution. The salts of the two elements should be purified as far as possible by fractional crystallizations.

*Experiment 2. Preparation of niobic and tantallic oxides (acids), ( $\text{Nb}_2\text{O}_5$ ;  $\text{Ta}_2\text{O}_5$ ).* (a) Evaporate to dryness in a lead or platinum dish a solution of potassium and niobium oxyfluoride, add strong sulphuric acid, and heat until all the hydrofluoric acid is expelled and a solution is obtained. Cool the solution, dilute with water, and boil. Niobic acid, ( $\text{Nb}_2\text{O}_5$ ), is precipitated. Filter, and test the filtrate with ammonium hydroxide.

(b) Repeat the experiment, using a solution of potassium and tantalum fluoride instead of the niobium salt.

(c) Test the action of alkali hydroxides or carbonates in excess upon solutions of niobium and tantalum obtained in (a) and (b).

(d) Try the action of the common acids upon freshly precipitated niobic and tantallic acids. Note that hydrogen dioxide aids the solvent action.

*Experiment 3. Effect of fusion with sodium or potassium hydroxide upon niobic and tantallic acids.* (a) Melt a gram of sodium or potassium hydroxide in a hard glass tube, add a small quantity of dry niobic acid, and heat again. Note that the fused mass is soluble in water.

(b) Repeat the experiment, using dry tantalic acid instead of niobic.

(c) Acidify with the common acids portions of the solutions obtained in (a) and (b).

(d) Try the effect of carbon dioxide upon these solutions.

*Experiment 4. Tests for niobium.* (a) To separate portions of dry niobic oxide (or acid) add a few drops of strong sulphuric acid, and treat with tannic acid, pyrogalllic acid, and morphia, respectively. Note the brown color.

(b) Repeat the experiment, using tantalic oxide instead of niobic. Note the absence of color.

(c) Try the action of metallic zinc upon an acid solution containing niobium. Note the color. Filter, and add a solution of mercuric chloride. Note the precipitate.

*Experiment 5. Negative tests of niobium and tantalum.* Note that hydrogen sulphide gives no precipitate, and that hydrogen peroxide gives no yellow color with acid solutions containing niobium or tantalum.

## CHAPTER VIII.

### MOLYBDENUM, Mo, 96.

**Discovery.** The name Molybdena, derived from *μόλυβδος*, *lead*, was originally applied to a variety of substances containing lead. Later the term was used to designate only graphite and a mineral sulphide of molybdenum which is very similar in appearance to graphite, and which was confused with it. In 1778 Scheele, in his treatise on molybdena (Kong. Vet. Acad. Handl. (1778), 247), showed that it differs from plumbago, or graphite, in that on being heated with nitric acid it yields a peculiar white earth, which he proved to be an acid-forming oxide. This he called "acidum molybdenæ," and he supposed the mineral to be a compound of this oxide with sulphur. In 1790 Hjelm (ibid. (1790), 50; Ann. de Chim. iv, 17) isolated the element.

**Occurrence.** Molybdenum occurs in combination in minerals which are somewhat widely diffused, though found in small amounts:

	Contains MoO <sub>3</sub>
Molybdic ocher or	
Molybdite, $\text{Fe}_2\text{O}_3 \cdot 3\text{MoO}_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$ .....	57-59%
Powellite, $\text{Ca}(\text{Mo}, \text{W})\text{O}_4$ .....	58-59%
<i>Wulfenite</i> , $\text{PbMoO}_4$ .....	37-40%
Belonesite, $\text{MgMoO}_4?$ .....	78-79%
Pateraite, $\text{CoMoO}_4?$ .....	30%
Scheelite, $\text{CaWO}_4$ .....	traces-8%
<i>Molybdenite</i> , $\text{MoS}_2$ .....	60% Mo
Ilsemanite, $\text{MoO}_2 \cdot 4\text{MoO}_3$ .....	68% Mo

**Extraction.** Molybdenum salts are usually obtained from molybdenite, the most abundant ore, though sometimes from other minerals. The following processes will illustrate the methods employed.

(1) *From molybdenite.* The mineral is roasted until sulphur dioxide is no longer given off and the residue is yellow when hot and white when cold. This residue is dissolved in dilute ammonium hydroxide, and the solution is evaporated to crystallization. Heat drives off the ammonia from the crystals and leaves the trioxide of molybdenum.

(2) *From molybdenite.* The mineral is treated with nitric acid (*vid.* Experiment 1).

(3) *From wulfenite.* The mineral is fused with potassium polysulphide. Upon extraction with water the lead remains insoluble, as the sulphide, and the molybdenum goes into solution as the sulpho salt. The filtrate is acidified with sulphuric acid, and the sulphide of molybdenum is precipitated (Wittstein).

**The Element.** *A. Preparation.* Elementary molybdenum may be prepared (1) by passing dry hydrogen over either the trioxide or the ammonium salt at red heat, (*vid.* Experiment 6); (2) by reducing the chlorides with hydrogen; (3) by heating the oxide ( $\text{MoO}_3$ ) with "misch-metal"; (4) by heating the oxide ( $\text{MoO}_2$ ) with aluminum (Goldschmidt process).

*B. Properties.* Molybdenum is a gray metallic powder, which is unchanged in the air at ordinary temperatures, but which, when heated, passes gradually into the trioxide. It is insoluble in hydrochloric, hydrofluoric, and dilute sulphuric acids, but soluble in nitric and concentrated sulphuric acids, in aqua regia, in chlorine water, and in melted potassium hydroxide, and potassium nitrate. Its specific gravity is 8.6.

**Compounds.\*** *A. Typical forms.* The following are typical compounds of molybdenum:

Oxides.....	MoO	Mo <sub>2</sub> O <sub>3</sub>	MoO <sub>2</sub>	Mo <sub>2</sub> O <sub>3</sub>	Mo <sub>2</sub> O <sub>5</sub>	MoO <sub>3</sub>
Chlorides....	MoCl <sub>2</sub>	MoCl <sub>3</sub>	MoCl <sub>4</sub>		MoCl <sub>5</sub>	
Oxychlorides.						MoOCl <sub>2</sub> MoO <sub>2</sub> Cl <sub>2</sub>
Bromides....	MoBr <sub>2</sub>	MoBr <sub>3</sub>	MoBr <sub>4</sub>			
Oxybromide..						MoO <sub>2</sub> Br <sub>2</sub>
Oxyiodide....					MoOI	
Fluoride.....						MoF <sub>6</sub>
Oxyfluorides.					MoOF <sub>5</sub> ·2KF + H <sub>2</sub> O	MoO <sub>2</sub> F <sub>2</sub> ·KF + H <sub>2</sub> O
Carbides.....	Mo <sub>2</sub> C		MoC			
Silicide.....			MoSi			
Sulphides....			MoS <sub>2</sub>			MoS <sub>3</sub> ; MoS <sub>4</sub>
Sulpho salt...						<sup>I</sup> R <sub>2</sub> MoS <sub>4</sub>

Molybdates, many salts of the type <sup>I</sup>R<sub>2</sub>MoO<sub>4</sub>, as K<sub>2</sub>MoO<sub>4</sub>; CaMoO<sub>4</sub>; ZnMoO<sub>4</sub>; Ag<sub>2</sub>MoO<sub>4</sub>; etc. The formula for ammonium molybdate is given as (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O. Barbieri has formed a series of molybdates of the rare earths of the type (NH<sub>4</sub>)<sub>3</sub>R<sup>III</sup>Mo<sub>7</sub>O<sub>24</sub>·12H<sub>2</sub>O, where R = Ce, La, Nd, Pr, or Sm.

Molybdenum trioxide combines with phosphoric pentoxide in the following proportions: P<sub>2</sub>O<sub>5</sub>:MoO<sub>3</sub>::1:24, 1:22, 1:20, 1:18, 1:16, 1:15, 1:5, as 2K<sub>2</sub>HPO<sub>4</sub>·24MoO<sub>3</sub>+3H<sub>2</sub>O; 2(NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>·16MoO<sub>3</sub>+14H<sub>2</sub>O; etc. It combines with arsenic pentoxide as follows: As<sub>2</sub>O<sub>5</sub>:MoO<sub>3</sub>::1:20, 1:18, 1:16, 1:6, 1:2, as As<sub>2</sub>O<sub>5</sub>·20MoO<sub>3</sub>+27H<sub>2</sub>O; 10NH<sub>3</sub>·As<sub>2</sub>O<sub>5</sub>·16MoO<sub>3</sub>+14H<sub>2</sub>O; etc.

*B. Characteristics.* The molybdenum compounds are known in various conditions of oxidation (*vid.* Typical

\* See also Bailhache, Compt. rend. cxxxv, 862; Mylius, Ber. Dtsch. chem. Ges. xxxvi, 638; Rosenheim, Zeitsch. anorg. Chem. xxxiv, 427; xlvi, 311; xlix, 148; l, 320; liv, 97; Grossmann, Zeitsch. anorg. Chem. xli, 43; Zeitsch. phys. Chem. lvi, 577; liv, 40; Weinland, Zeitsch. anorg. Chem. xlv, 81; Sand, Ber. Dtsch. chem. Ges. xxxviii, 3384; xl, 4504; Copaux, Ann. chim. phys. [8] vii, 118; Bull. Soc. franç. Minéral. xxx, 292 (Oct. 1907), or Chem. Zentr. (1908) i, 1711; Lancien, Bull. d. Sciences Pharmacol. xv, 132, or Chem. Zentr. (1908) i, 1763; Ruff, Ber. Dtsch. chem. Ges. xl, 2926.

known in various conditions of oxidation (*vid.* Typical Forms), of which the highest,  $(\text{MoO}_3)$ , is the most stable and comprises the largest number of salts. The trioxide is white to pale yellow, and dissolves in potassium, sodium, and ammonium hydroxides, forming the molybdates. These alkali molybdates are the chief soluble salts. When strong reducing agents, such as zinc and hydrochloric acid, act upon acid solutions of molybdates, the reduction is said to go as far as the oxide  $\text{Mo}_5\text{O}_7$ , the solution passing through the colors of the various oxides, violet, blue, and black. The oxide  $\text{Mo}_5\text{O}_7$ , however, is very sensitive to oxidation, for it is changed in the air to the sesquioxide ( $\text{Mo}_2\text{O}_3$ ) as soon as the reducing action has ceased. Acid solutions of the lower oxides give, on treatment with the alkali hydroxides, the corresponding hydroxides of molybdenum,  $\text{Mo}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ;  $\text{MoO}_2 \cdot x\text{H}_2\text{O}$ ; etc. The sulphide ( $\text{MoS}_2$ ) is obtained by treating a molybdate with ammonium sulphide and acidifying. Its color is reddish brown.

**Estimation.\*** *A. Gravimetric.* Molybdenum is generally weighed as the oxide ( $\text{MoO}_3$ ), obtained (1) by ignition of ammonium molybdate; (2) by precipitation of mercury molybdate and ignition; or (3) by precipitation of the sulphide and conversion into the oxide by treatment with nitric acid.

*B. Volumetric.* Soluble molybdates may be reduced in acid solution (1) by boiling with potassium iodide. (a) The iodine thus liberated may be passed into potassium iodide and estimated by standard thiosulphate, the amount of molybdenum present being calculated from the equation  $2\text{MoO}_3 + 2\text{HI} = \text{Mo}_2\text{O}_5 + \text{I}_2 + \text{H}_2\text{O}$ ; or, (b) after the iodine has been removed by boiling, the residual solution may be rendered alkaline by potassium bicarbonate and reoxidized

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\* For the estimation in ores, see Low's *Technical Methods of Ore Analysis*; Blair, *Jour. Amer. Chem. Soc.* xxx, 1229.

by standard iodine solution or potassium permanganate (Mauro and Danesi, *Zeitsch. anal. Chem.* xx, 507; Friedheim and Euler, *Ber. Dtsch. chem. Ges.* xxviii, 2066; Gooch and Fairbanks, *Amer. Jour. Sci.* [4] ii, 156; Gooch and Pulman, *Amer. Jour. Sci.* [4] xii, 449); (2) by passing the solution over zinc in a Jones reductor into a flask charged with a ferric salt. The molybdic acid, reduced to the sesquioxide ( $\text{Mo}_2\text{O}_3$ ) in the reductor is reoxidized by the ferric salt, and the ferrous salt formed is titrated by permanganate (Randall, *Amer. Jour. Sci.* xxiv (1907), 313). See also under Vanadium a volumetric process for the estimation of vanadium and molybdenum in the presence of each another, page 112.

**Separation.** The general methods for the separation of molybdenum from the metals and alkali earths are the same as those described under Vanadium.

From arsenic and phosphorus, when present as arsenic and phosphoric acids, molybdenum may be separated by magnesium chloride mixture in ammoniacal solution, ammonium-magnesium arseniate and phosphate being precipitated (Gibbs, *Amer. Chem. Jour.* vii, 317; Gooch, *Amer. Chem. Jour.* i, 412).

For the separation from vanadium, *vid.* Vanadium.

From tungsten molybdenum may be separated (1) by the action of warm sulphuric acid of specific gravity 1.37 upon the oxides ( $\text{MoO}_3$  and  $\text{WO}_3$ ), molybdic acid dissolving (Ruegenberg and Smith, *Jour. Amer. Chem. Soc.* xxii, 772); (2) by heating the oxides with hydrochloric-acid gas at  $250^\circ$ – $270^\circ$  C., the molybdenum compound ( $\text{MoO}_3 \cdot 2\text{HCl}$ ) being volatilized (Pechard, *Compt. rend.* cxiv, 173; Debray, *ibid.* xlvi, 1101); (3) by precipitation of the sulphide of molybdenum by means of hydrogen sulphide in the presence of tartaric acid (Rose, *Handbuch der anal. Chemie* (sechste Auflage, 1871), 358).



## EXPERIMENTAL WORK ON MOLYBDENUM.

*Experiment 1. Extraction of molybdenum salts from molybdenite, ( $\text{MoS}_2$ ).* Heat 5 grm. of the finely powdered mineral with nitric acid until the dark color has disappeared. Evaporate to dryness, wash the residue in warm dilute nitric acid, then in water, and dissolve it in ammonium hydroxide. Filter, and evaporate the filtrate to a small volume. Ammonium molybdate crystallizes out, which may be converted into the trioxide by careful ignition.

*Experiment 2. Precipitation of the sulphides of molybdenum, ( $\text{MoS}_2$ ;  $\text{MoS}_3$ ).* (a) Through a solution of ammonium molybdate acidified with hydrochloric acid pass hydrogen sulphide. Note the gradual change of color of the solution, from red-brown to blue, and the partial precipitation of the sulphide  $\text{MoS}_2$ .

(b) To a solution of ammonium molybdate add ammonium sulphide, or pass hydrogen sulphide through an alkaline solution of a molybdate. Note the yellow-brown color ( $(\text{NH}_4)_2\text{MoS}_4$ , typical). Acidify the solution and note the brown precipitate ( $\text{MoS}_3$ ).

*Experiment 3. Precipitation of ammonium phosphomolybdate ( $3(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 24(\text{MoO}_3) + 2\text{H}_2\text{O}$ ).* To a solution of ammonium molybdate acidified with nitric acid add a drop of a solution of sodium phosphate, and warm gently. Note the yellow precipitate.

*Experiment 4. Precipitation of the molybdates of silver, lead, and barium, ( $\text{Ag}_2\text{MoO}_4$ ,  $\text{PbMoO}_4$ , and  $\text{BaMoO}_4$ , typical).* To separate solutions of ammonium molybdate, neutral or faintly acid with acetic acid, add solutions of silver nitrate, lead acetate, and barium chloride respectively. Note the solvent action of nitric acid upon the precipitates.

*Experiment 5. Reduction of molybdic acid, ( $\text{MoO}_3$ ).*

(a) Put a piece of metallic zinc into a solution of ammonium molybdate and add hydrochloric acid until the action starts. Note the change in color of the solution as the reduction proceeds (reddish yellow, violet, bluish, black). To a few drops of the solution after reduction add potassium or sodium hydroxide. Note the dark-brown precipitate of the lower hydroxides of molybdenum ( $\text{Mo}_2(\text{OH})_6$ , etc.) mixed with the hydroxide of zinc.

(b) Try the reducing action of stannous chloride upon a molybdate in solution.

(c) To a dilute solution of a molybdate which has been treated with zinc and hydrochloric acid, add some potassium sulphocyanide in solution. Note the red color. Try the effect of adding ether and shaking.

(d) To a few drops of a solution of a molybdenum compound add a little strong sulphuric acid, and evaporate nearly to dryness in a porcelain dish. Note the blue color.

(e) To a solution of a molybdenum compound add a little diphenylcarbazid. Note the indigo blue color.

(f) Try the effect of phenylhydrazin, tannic, gallic, and pyrogallac acids upon molybdenum solutions. Note the colors—deep red in the first instance and orange to red in the others.

*Experiment 6. Preparation of elementary molybdenum from ammonium molybdate.* Heat a few grams of finely powdered ammonium molybdate until no further test for ammonia is obtained when a piece of moistened red litmus paper is held over the substance. Remove the molybdic trioxide thus obtained to a Rose crucible and heat for some time in a current of hydrogen. Note the gray powder.

## TUNGSTEN, W. 184.

**Discovery.** The minerals scheelite, formerly called tungsten (i.e. "heavy stone"), and wolframite have long been known, but until about the middle of the eighteenth century they were regarded as tin ores. In 1781 Scheele (Kong. Vet. Acad. Handl. (1781), 89) demonstrated that scheelite contained a peculiar acid which he named Tungstic acid. Two years later the brothers D'Elhujar showed the presence of the same acid in wolframite.

**Occurrence.** Tungsten is found combined in minerals which are often associated with tin ores:

	Contains WO <sub>3</sub> .
<i>Wolframite</i> , (Fe,Mn)WO <sub>4</sub> .....	74-78%
<i>Scheelite</i> , CaWO <sub>4</sub> .....	71-80%
<i>Hübnerite</i> , MnWO <sub>4</sub> .....	73-77%
<i>Cuprotungstite</i> , CuWO <sub>4</sub> .....	56-57%
<i>Cuproscheelite</i> , (Ca,Cu)WO <sub>4</sub> .....	76-80%
<i>Powellite</i> , Ca(Mo,W)O <sub>4</sub> .....	10-11%
<i>Stolzite</i> , PbWO <sub>4</sub> .....	51 <i>circa</i>
<i>Raspite</i> , PbWO <sub>4</sub> .....	49 "
<i>Reinite</i> , FeWO <sub>4</sub> .....	75-76%
<i>Ferberite</i> , FeWO <sub>4</sub> .....	69-70%
<i>Yttrotantalite</i> , complex niobate-tantalate.....	2- 4%
<i>Tungstite</i> , WO <sub>3</sub> .....	100 <i>circa</i>
<i>Meymacite</i> , hydrated WO <sub>3</sub> .....	71-75%

**Extraction.\*** Tungstic acid is usually extracted from wolframite. Any of the processes here indicated may be followed:

(1) 5 parts of the mineral are fused with 8.5 parts of dry sodium carbonate and 1.5 parts of sodium nitrate. On treatment of the fused mass with water, sodium tung-

\* See also an interesting discussion of the treatment of tungsten ores, etc., by Van Wegenen, *The Chemical Engineer*, Vol. IV, 217-232 and 284-297.

state is dissolved, and after filtration tungstic acid is precipitated by hydrochloric acid.

(2) The mineral is fused with an equal weight of calcium carbonate and one-half of its weight of sodium chloride, and the melt is treated with hot water containing hydrochloric and nitric acids. The tungstic acid remains undissolved.

(3) The mineral is decomposed by hydrochloric acid (*vid.* Experiment 1).

**The Element.** *A. Preparation.\** Elementary tungsten may be obtained (1) by heating the acid in the presence of hydrogen; (2) by heating the chloride ( $WCl_6$ ) in the presence of hydrogen; (3) by heating the acid with carbon; (4) by heating the nitride; (5) by passing an electric current *in vacuo* through filaments of an amalgam of tungsten, cadmium, and mercury, the cadmium and mercury being expelled and the tungsten left; (6) by heating the acid with metallic zinc (Weiss).

*B. Properties.\** Tungsten is a very hard powder, ranging in color from gray to brownish black, resembling sometimes tin, sometimes iron. Although unchanged in the air at ordinary temperatures, when heated in finely divided condition it ignites and burns to the oxide ( $WO_3$ ). Its melting-point is variously given as  $2650^\circ$  (Ruff),  $2850^\circ$  (Weiss),  $2900^\circ$  (v. Wartenburg). It is slowly attacked when heated with sulphuric or nitric acid; and readily attacked by a mixture of nitric and hydrofluoric acids, forming  $WF_6$  or  $WOF_4$ , and by fusion with alkalis and saltpeter. It is acted upon also by dry chlorine at high temperatures. The specific gravity of tungsten is from 16.5 to 19.1. Weiss gives 18.7.

**Compounds.†** *A. Typical forms.* The following compounds of tungsten may be considered typical:

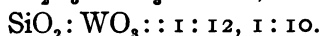
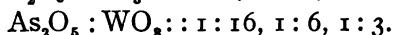
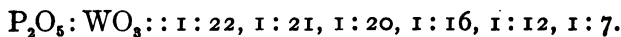
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\* See Weiss, *Zeitsch. anorg. Chem.* LXV, 279.

† See also Rosenheim, *Zeitsch. anorg. Chem.* LIV, 97.

Oxides * .....	WO <sub>3</sub>	WO <sub>3</sub>
Chlorides .....	WCl <sub>3</sub> WCl <sub>4</sub> WCl <sub>5</sub>	WCl <sub>4</sub>
Oxychlorides .....		WOCls WO <sub>2</sub> Cl <sub>3</sub>
Bromides .....	WBr <sub>3</sub> WBr <sub>4</sub>	
Oxybromides .....		WOBr <sub>4</sub> WO <sub>2</sub> Br <sub>2</sub>
Iodide .....	WI <sub>3</sub>	
Fluoride .....		WF <sub>6</sub>
Double fluorides ..	KF · WO <sub>3</sub> F + H <sub>2</sub> O	ZnF <sub>2</sub> · WO <sub>3</sub> F <sub>2</sub> + 10H <sub>2</sub> O; etc.
Carbide .....	WC	
Silicide .....	WSi <sub>2</sub>	
Sulphides .....	WS <sub>2</sub>	WS <sub>2</sub>
Sulpho salts .....		R <sub>2</sub> WS <sub>4</sub> R <sub>2</sub> WS <sub>2</sub> O <sub>2</sub> R <sub>2</sub> WSO <sub>2</sub>
Tungstates, many salts of the types		R <sub>2</sub> WO <sub>4</sub> (normal) R <sub>2</sub> W <sub>4</sub> O <sub>13</sub> (meta) R <sub>4</sub> W <sub>7</sub> O <sub>24</sub> (para)

Tungstic trioxide (acid) combines with phosphoric pentoxide, arsenic pentoxide, and silicon dioxide in the following proportions:



*B. Characteristics.* The compounds of tungsten are very similar to those of molybdenum, and are known in several conditions of oxidation (*vid.* Typical Forms), of which the highest is the most stable. The trioxide, (WO<sub>3</sub>), united with the bases, forms the largest number of salt- the tungstates. The alkali tungstates are the chief soluble salts. When acted upon by reducing agents, tungstic acid or trioxide may be reduced to the dioxide, (WO<sub>2</sub>), the solution becoming blue, then brown. When the solution of a tungstate is acidified, tungstic acid is precipitated.

\* Some authorities give three oxides between the dioxide and the trioxide, viz., W<sub>2</sub>O<sub>6</sub>, W<sub>3</sub>O<sub>8</sub>, and W<sub>4</sub>O<sub>11</sub>.

Tungstic sulphide, ( $WS_3$ ), is obtained under the same conditions as molybdenum sulphide, and is brown. It dissolves in ammonium sulphide, forming a sulpho salt.

**Estimation.\*** Tungsten is ordinarily weighed as the oxide ( $WO_3$ ), obtained (1) by igniting ammonium tungstate; (2) by decomposing the alkali tungstates with nitric acid, evaporating to dryness, and extracting with water,—tungstic acid remaining undissolved; (3) by precipitating mercury tungstate and driving off the mercury by means of heat, leaving the acid or oxide; (4) by boiling fused lead tungstate with strong hydrochloric acid,—tungstic acid being precipitated (Brearley, Chem. News LXXIX, 64).

**Separation.** Tungsten may be separated from the metallic bases and many other elements by the following process: fusion with an alkali carbonate, extraction of the alkali tungstate with water, acidification with nitric acid, evaporation to dryness, and extraction with water,—tungstic acid remaining undissolved.

For the separation of tungsten from molybdenum and vanadium, see those elements. From arsenic and phosphorus tungsten is separated by magnesium mixture (Gooch, Amer. Chem. Jour. 1, 412; Gibbs, Amer. Chem. Jour. VII, 337).

From tin the separation may be accomplished (1) by ignition with ammonium chloride, tin chloride being volatilized (Rammelsberg); (2) by fusion with potassium cyanide, the tin being reduced to the metal and the tungsten being converted into a soluble tungstate (Talbot).

## EXPERIMENTAL WORK ON TUNGSTEN.

*Experiment 1. Extraction of tungstic acid from wolframite* ( $(Fe,Mn)WO_4$ ). Treat 5 grm. of the finely powdered mineral with about 10 cm.<sup>3</sup> of a mixture of equal parts of hydrochloric acid and water, and boil as long as any action

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\* For the estimation in ores see Low's Technical Methods of Ore Analysis.

seems to take place. Decant the solution, add to the residue about 10 cm.<sup>3</sup> of a mixture of nitric and hydrochloric acids (aqua regia), and warm. Add more acid if necessary, and continue this treatment until the residue is yellow; filter, and wash with dilute hydrochloric acid and then with water. Warm the yellow mass with ammonium hydroxide as long as any solvent action is observed, and filter. Evaporate the filtrate to dryness and ignite the ammonium tungstate to obtain tungstic acid.

*Experiment 2. Formation of sodium tungstate and metatungstate* ( $\text{Na}_2\text{WO}_4$  and  $\text{Na}_2\text{W}_4\text{O}_{13}$ , typical). (a) Dissolve a little tungstic acid in a solution of sodium carbonate.

(b) Dissolve a little tungstic acid in a solution of sodium tungstate.

*Experiment 3. Precipitation of tungstic sulphide* ( $\text{WS}_3$ ), and formation of the sulpho salt ( $(\text{NH}_4)_2\text{WS}_4$ ). (a) To a solution of sodium or ammonium tungstate add ammonium sulphide, and acidify with hydrochloric acid.

(b) Try the action of hydrogen sulphide upon a soluble tungstate.

(c) Try the action of ammonium sulphide upon tungstic sulphide.

*Experiment 4. Precipitation of tungstic acid* ( $\text{WO}_3$ ). Acidify a concentrated solution of a tungstate with hydrochloric or nitric acid and boil. Try the action of nitric and hydrochloric acids upon a tungstate in the presence of tartaric acid.

*Experiment 5. Precipitation of barium, lead, and silver tungstates* ( $\text{R}_2\text{WO}_4$ , typical). To separate portions of a solution of sodium tungstate acidified with acetic acid add solutions of barium, lead, and silver salts respectively.

*Experiment 6. Reduction of tungstic acid.* (a) To a solution of a tungstate (e.g., sodium tungstate) add a solution of stannous chloride. Acidify with hydrochloric acid and warm gently. (b) To a solution of a tungstate add zinc and hydrochloric acid and warm gently.

and warm gently. (b) To a solution of a tungstate add zinc and hydrochloric acid and warm gently.

*Experiment 7. Salt of phosphorus bead tests.* Make a bead of microcosmic salt, and heat it in the oxidizing and reducing flames with a small particle of tungstic acid. Try the effect of a small amount of ferrous sulphate upon the bead heated in the reducing flame.

### URANIUM,\* U, 238.5.

**Discovery.** Klaproth, in the year 1789, discovered that the mineral pitch-blende, supposed to be an ore of zinc, iron, or tungsten, contained a "half-metallic substance" differing in its reactions from all three (Crell Annal. (1789) II, 387). This he named Uranium in honor of Herschel's discovery of the planet Uranus in 1781. The body that Klaproth obtained was really an oxide of uranium, as Péligré showed in 1842, when he succeeded in isolating the metal (Ann. de Chim. (1842) v, 5).

**Occurrence.** Uranium is found combined in a few minerals, most of them rare. Pitch-blende is the most abundant source.

<i>Uraninite (pitch-blende)</i> , $\text{UO}_2 \cdot \text{UO}_3 \cdot \text{PbO} \cdot \text{N}$ , etc., contains	75-85% ( $\text{UO}_2 + \text{UO}_3$ )
Bröggerite, <i>vid.</i> Uraninite,	" 76-79% "
Cleveite, <i>vid.</i> Uraninite,	" 66% "
Nivenite, <i>vid.</i> Uraninite,	" 67% "
Thorianite, $\text{ThO}_2 \cdot \text{U}_3\text{O}_8$ ,	" 12-25% U
<i>Gummite</i> , $(\text{Pb}, \text{Ca})\text{U}_3\text{SiO}_{12} \cdot 6\text{H}_2\text{O}?$ ,	" 61-75% $\text{UO}_3$
Thorogummite, $\text{UO}_2 \cdot 3\text{ThO}_2 \cdot 3\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ ,	" 22-23% "
Pilbarite, $\text{PbO} \cdot \text{UO}_2 \cdot \text{ThO}_2 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} + 2\text{H}_2\text{O}$ ,	" 27.09% "
Mackintoshite, $\text{UO}_2 \cdot 3\text{ThO}_2 \cdot 3\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ ,	" 21-22% $\text{UO}_3$
Uranophane, $\text{CaO} \cdot 2\text{UO}_3 \cdot 2\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ ,	" 53-67% $\text{UO}_3$
Naegite, † silicate,	" 28-29% $\text{UO}_3$
<i>Uranosphaerite</i> , $(\text{BiO})_2\text{U}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ ,	" 50-51% $\text{UO}_3$
Walpurgite, $\text{Bi}_{10}(\text{UO}_2)_3(\text{OH})_{24}(\text{AsO}_4)_4$ ,	" 20-21% "
<i>Carnotite</i> , $\text{K}_2\text{O} \cdot 2\text{U}_2\text{O}_5 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}?$ ,	" 62-65% $\text{U}_2\text{O}_5$
<i>Torbernite</i> , $\text{Cu}(\text{UO}_2)_2\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$ ,	" 57-62% $\text{UO}_3$
<i>Zeunerite</i> , $\text{Cu}(\text{UO}_2)_2\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$ ,	" 55-56% "
<i>Autunite</i> , $\text{Ca}(\text{UO}_2)_2\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$ ,	" 55-62% "

\* For a discussion of radioactive properties, see Chapter III.

† A Japanese mineral, Chem. Zentr. (1905) I, 763.



Uranospinite, $\text{Ca}(\text{UO}_2)_2\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$ ,	contains 59-60% $\text{UO}_2$
Uranocircite, $\text{Ba}(\text{UO}_2)_2\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$ ,	" 56-57% "
Johannite, sulphate, formula doubtful,	" 67-68% "
Uranopilite, $\text{CaO} \cdot 8\text{UO}_2 \cdot 2\text{SO}_3 \cdot 25\text{H}_2\text{O}$ ,	" 77-78% "
Uranochalcite, <i>vid.</i> Uranopilite,	" 36% $\text{U}_2\text{O}_4$
Zippeite, <i>vid.</i> Uranopilite,	" 13-14% "
Voglianite, <i>vid.</i> Uranopilite,	" 12% "
Uraconite, <i>vid.</i> Uranopilite,	" 66-71% "
Thorite, $\text{ThSiO}_4$ ,	" 1-10% $\text{UO}_2$
Phosphuranylite, $(\text{UO}_2)_3\text{P}_2\text{O}_8 \cdot 6\text{H}_2\text{O}$ ,	" 72-77% "
Trögerite, $(\text{UO}_2)_2\text{As}_2\text{O}_8 \cdot 12\text{H}_2\text{O}$ ,	" 63-64% "
Rutherfordite, $\text{UO}_2\text{CO}_3$ ,	" 80-84% "
Uranothallite, $2\text{CaCO}_3 \cdot \text{U}(\text{CO}_3)_2 \cdot 10\text{H}_2\text{O}$ ,	" 35-37% $\text{UO}_2$
Liebigite, $\text{CaCO}_3 \cdot (\text{UO}_2)\text{CO}_3 \cdot 20\text{H}_2\text{O}$ ,	" 36-38% $\text{UO}_2$
Voglite, complex carbonate,	" 37% $\text{UO}_2$
Hatchettolite, $\text{R}(\text{Nb}, \text{Ta})_2\text{O}_6 \cdot \text{H}_2\text{O}$ ,	" 15-16% $\text{UO}_2$
Fergusonite, $\text{R}(\text{Nb}, \text{Ta})\text{O}_4$ ,	" 0-8% $\text{UO}_2$
Sipylite, complex niobate,	" 3-4% "
Samarskite, $\text{R}_2\text{R}_2(\text{Nb}, \text{Ta})_6\text{O}_{21}$ ,	" 10-13% $\text{UO}_2$
Nohlite, <i>vid.</i> Samarskite,	" 14% $\text{UO}$
Vetringhofite, <i>vid.</i> Samarskite,	" 9% $\text{U}_2\text{O}_3$
Ainnerödite, complex,	" 16-17% $\text{UO}_2$
Hielmite, complex,	" 0-5% "
Euxenite, $\text{R}(\text{NbO}_3)_2 \cdot \text{R}_2(\text{TiO}_3)_2 \cdot \frac{3}{2}\text{H}_2\text{O}$ ,	" 5-12% "
Polycrase, $\text{R}(\text{NbO}_3)_2 \cdot 2\text{R}(\text{TiO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,	" 1-19% "
Yttrocrasite, complex,	" 2-3% "
Blomstrandite, tantalum-niobate,	" 23% $\text{UO}$
Xenotime, $\text{YPO}_4$ ,	" 4% $\text{UO}_2$

**Extraction.** Uranium salts may be extracted from pitchblende as follows:

(1) The mineral is decomposed with nitric acid, the acid solution is evaporated to dryness, and the mass is extracted with water. The residue, which consists largely of lead sulphate, iron arseniate, and iron oxide, is filtered off, and on evaporation of the solution impure nitrate of uranium crystallizes out, which may be purified by recrystallization (Péligot).

(2) The mineral is decomposed by aqua regia (*vid.* Experiment 1).

**The Element. A. Preparation.** Metallic uranium may be obtained (1) by heating a mixture of the chloride  $\text{UCl}_3$  with sodium and potassium chloride in a porcelain crucible surrounded by powdered carbon contained in another crucible (Péligot); (2) by heating the oxide ( $\text{U}_3\text{O}_8$ ) with sugar carbon in a carbon tube (Moissan).

**B. Properties.** Uranium is a somewhat malleable white metal with much the appearance of nickel. Heated in air or oxygen to a temperature of  $150^\circ$ – $170^\circ$  C. it burns to the oxide; at ordinary temperatures the oxidation takes place slowly. Uranium dissolves slowly in cold dilute sulphuric acid, and more rapidly upon the application of heat. It is soluble in nitric and hydrochloric acids. It is attacked by chlorine at  $150^\circ$  C. and by bromine at  $240^\circ$  C. The caustic alkalis have no apparent action upon the element. The specific gravity of uranium is 18.6.

**Compounds.\* A. Typical forms.** The following are typical compounds of uranium:

Oxides† . . . . .	$\text{UO}_2$	$\text{U}_3\text{O}_8(\text{UO}_2 + 2\text{UO}_3)$	$\text{UO}_3$
Carbonates. . . . .			$\text{UO}_2\text{CO}_3 \cdot 2\text{K}_2\text{CO}_3$ $\text{UO}_2\text{CO}_3 \cdot 2(\text{NH}_4)_2\text{CO}_3$
Chlorides. . . . .	$\text{UCl}_3$	$\text{UCl}_4$	$\text{UCl}_5$
Bromides. . . . .	$\text{UBr}_3$	$\text{UBr}_4$	$\text{UBr}_5$
Iodide. . . . .		$\text{UI}_4$	
Iodate. . . . .			$\text{UO}_2(\text{IO}_3)_2$
Fluorides. . . . .	$\text{UF}_3$	$\text{UF}_4$	$\text{UF}_5$
		$\text{UOF}_2$	$\text{UO}_2\text{F}_2$
			$\text{UO}_2\text{F}_2 \cdot \text{NaF}$ , etc.
Sulphides. . . . .	$\text{US}$	$\text{U}_2\text{S}_3$	$\text{US}_2$
		$\text{US}_2$	$\text{UO}_2\text{S}$
			$\text{UO}_2\text{SO}_4 + 3\frac{1}{2}\text{H}_2\text{O}$
Sulphates. . . . .	$\text{UH}(\text{SO}_4)_2$	$\text{U}(\text{SO}_4)_2 + 4\text{H}_2\text{O}$	

\* See also Giolitti, Gazz. chim. ital. xxxv [II], 145, 151, 162, 170; Colani, Ann. Chim. Phys. [8] xii, 59–144 (1907); Mazzucchelli, Atti R. Accad. dei Lincei, Roma [5] xvi [II], 576; also Chem. Zentr. (1908) 1, 218; Lancien, Chem. Zentr. (1908) 1, 1763; Aloy, Chem. Zentr. (1907) II, 883.

† Other oxides less well known than those given above are of the following forms:  $\text{UO}$ ,  $\text{U}_2\text{O}_3$ ,  $\text{U}_3\text{O}_6$ , and  $\text{UO}_4$ .

Nitrate. ....		$\text{UO}_2(\text{NO}_3)_2 + 6\text{H}_2\text{O}$
Nitride. ....	$\text{U}_3\text{N}_4$	
Ferrocyanides. . .	$\text{UFe}(\text{CN})_6$	$(\text{UO}_2)_3\text{K}_2(\text{FeC}_6\text{N}_6)_2$
Phosphates, ortho.	$\text{UOHPO}_4$	$(\text{UO}_2)_2\text{H}_2(\text{PO}_4)_4$
pyro..	$(\text{UO})_2\text{P}_2\text{O}_7$	$(\text{UO}_2)_2\text{P}_2\text{O}_7$
meta..	$\text{UO}(\text{PO}_3)_2$	$\text{UO}_2(\text{PO}_3)_2$
Arseniate. ....		$\text{UO}_2\text{HAsO}_4 + 4\text{H}_2\text{O}$
Uranates, of types $\text{R}_2\text{UO}_4$ , $\text{R}_2\text{U}_2\text{O}_7$ , and $\text{R}_4\text{UO}_6$ .		
Peruranates, $(\text{Na}_2\text{O})_2\text{UO}_4 \cdot 8\text{H}_2\text{O}$ ; $(\text{PbO})_2\text{UO}_4 \cdot \text{PbUO}_4$ .		

*B. Characteristics.* Uranium differs from molybdenum and tungsten in manifesting less marked acidic qualities. The chief classes of salts are the uranyl, in which uranium shows its highest degree of oxidation, corresponding to the oxide  $\text{UO}_3$  (e.g.,  $\text{UO}_2\text{Cl}_2$ ), and the uranous, of which the oxide  $\text{UO}_2$  is the type (e.g.,  $\text{UCl}_4$ ). The uranyl salts are the more stable and better known. They may be reduced by zinc and hydrochloric acid to the lower condition. The uranous salts are easily oxidized to the higher form. The uranyl salts are, in general, yellow, the uranous greenish. The two conditions of oxidation may be further distinguished by the following reactions: the precipitate resulting from the action of ammonium sulphide upon uranyl salts is reddish brown,—upon uranous salts, light green; the precipitate resulting from the action of potassium ferrocyanide upon uranyl salts is blood-red,—upon uranous salts yellowish green.

Uranates of the types  $\text{R}_2\text{UO}_4$  and  $\text{R}_2\text{U}_2\text{O}_7$  are formed by the combination of the oxide  $\text{UO}_3$  with the strong bases.

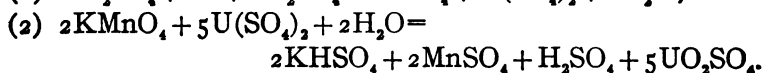
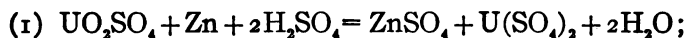
**Estimation.\*** *A. Gravimetric.* Uranium may be weighed (1) as urano-uranic oxide ( $\text{U}_3\text{O}_8$ ), obtained by precipitation of ammonium uranate by means of ammonia, and ignition in air or oxygen; (2) as urano-uranic oxide, precipitated electrolytically by a current of 0.18 ampere

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\* *Vid.* Kern, Jour. Amer. Chem. Soc. xxxiii, 685. For the estimation in ores, see Low's Technical Methods of Ore Analysis.

and 3 volts at a temperature of  $70^{\circ}$  C. (Smith and Wallace, Jour. Amer. Chem. Soc. xx, 279; Smith and Kollock, *ibid.* xxiii, 607); (3) as uranous oxide ( $\text{UO}_2$ ), obtained by ignition of urano-uranic oxide in a current of hydrogen; (4) as the pyrophosphate ( $(\text{UO}_2)_2\text{P}_2\text{O}_7$ ), obtained by precipitation by means of ammonium phosphate in the presence of ammonium acetate, and ignition.

*B. Volumetric.* Uranium may be estimated volumetrically by reduction from the higher ( $\text{UO}_3$ ) to the lower ( $\text{UO}_2$ ) condition of oxidation by means of zinc and sulphuric acid, and oxidation with permanganate, according to the following formulæ (Pulman, Amer. Jour. Sci. [4] xvi, 229):



**Separation.\*** From the metals which precipitate sulphides with hydrogen sulphide in acid solution, uranium may be separated by hydrogen sulphide. From iron, nickel, and other members of its own group it may be separated by ammonium sulphide in the presence of an excess of sodium or ammonium carbonate, the uranium salt remaining in solution. From the alkalis and alkali earths the separation may be accomplished by means of ammonium sulphide in the presence of ammonium chloride, uranium oxysulphide being precipitated.

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\* *Vid.* Kern, Jour. Amer. Chem. Soc. xxiii, 685. For the estimation in ores, see Low's Technical Methods of Ore Analysis.

## EXPERIMENTAL WORK ON URANIUM.

*Experiment 1. Extraction of uranium salts from pitch-blende.* Warm 5 grm. of pulverized pitch-blende with aqua regia until the decomposition is complete, and remove the excess of acid by evaporation. Extract with water and boil the solution a few minutes with sulphurous acid to reduce the arsenic acid. When the liquid is at about  $60^{\circ}\text{C.}$ , pass hydrogen sulphide through to the complete precipitation of arsenic, copper, lead, bismuth, and tin. Filter, oxidize the filtrate with nitric acid, and precipitate with ammonium hydroxide. Treat the precipitate with hot concentrated ammonium carbonate, filter, and allow the filtrate to cool. The double carbonate of uranium and ammonium will separate. A further precipitate, of crude ammonium uranate, may be obtained by boiling the mother-liquor. Uranium salts may be extracted from carnotite by the method described under Vanadium, Experiment 1, page 114, the sodium hydroxide precipitate being treated with hot concentrated ammonium carbonate, as directed above.

*Experiment 2. Precipitation of sodium, potassium, or ammonium uranate, ( $\overset{1}{\text{R}}_2\text{U}_2\text{O}_7$ , typical).* To a solution of a uranyl salt add sodium, potassium, or ammonium hydroxide. Note the yellow color of the precipitate and the insolubility in excess of the reagent. Repeat the experiment with hydrogen dioxide present in the solution.

*Experiment 3. Formation of the soluble double carbonates of uranium with sodium or potassium, and uranium with ammonium, ( $\text{UO}_2\text{CO}_3 \cdot 2\overset{1}{\text{R}}_2\text{CO}_3$ ).* (a) To a solution of a uranyl salt add a solution of sodium or potassium carbonate, noting the first and the final effects. Try the result of boiling, and of adding sodium or potassium hydroxide to a separate portion of the clear solution.

(b) Try similarly the action of ammonium carbonate upon a uranyl salt in solution. Note the ready solvent action of an excess of the carbonate, and the precipitation of ammonium uranate,  $((\text{NH}_4)_2\text{U}_2\text{O}_7)$ , on boiling.

(c) To a solution of a uranyl salt add hydrogen dioxide and potassium or sodium carbonate. Note the cherry-red color (Aloy).

*Experiment 4. Precipitation of uranyl ferrocyanide,  $((\text{UO}_2)_3\text{K}_2(\text{FeC}_6\text{N}_6)_2$  or  $(\text{UO}_2)_2\text{FeC}_6\text{N}_6$ ).* (a) To a very dilute solution of a uranyl salt add a little potassium ferrocyanide in solution. Note the red precipitate. This is a delicate test for uranyl salts. The precipitate, which is similar in color to that formed with cupric salts, may be distinguished from copper ferrocyanide by its decomposition on treatment with potassium hydroxide with the formation of yellow insoluble potassium uranate.

(b) Try similarly the action of potassium ferricyanide.

*Experiment 5. Precipitation of uranyl phosphate,  $(\text{UO}_2\text{HPO}_4)$ .* To a solution of a uranyl salt add a solution of hydrogen disodium phosphate. Try the action of the common acids upon the precipitate.

*Experiment 6. Precipitation of uranyl sulphide,  $(\text{UO}_2\text{S})$ .* (a) To a solution of a uranyl salt add ammonium sulphide. Note the dark-brown color of the precipitate, and the insolubility in excess of the reagent.

(b) Try the action of hydrogen sulphide upon a uranyl salt.

*Experiment 7. Reduction of uranyl salts.* (a) To a solution of a uranyl salt add zinc and sulphuric acid. Note the change of color from yellow to green.

(b) Bring about the reduction with magnesium and acid. Test the uranous salt in solution with potassium ferrocyanide and with ammonium sulphide.

*Experiment 8. Bead tests.* Fuse a little of a uranium salt in a borax or sodium metaphosphate bead. Note the yellow color in the oxidizing flame and green color in the reducing flame.

## CHAPTER IX.

### SELENIUM, Se, 79.2.

**Discovery.** For some time previous to the discovery of selenium a red deposit had been noticed in the lead chambers used in the manufacture of sulphuric acid at Gripsholm in Sweden. The deposit was present when the sulphur employed had been prepared from pyrites from Fahlun, Sweden, but was seldom observed when the sulphur had been obtained from other sources. At first the unknown substance was supposed to be sulphur. When it was burned, an odor as of decayed cabbage was given off, and this was supposed to be caused by the presence of tellurium sulphide, although no tellurium could be extracted from the material. In 1817 Berzelius, having become a shareholder in the acid works, examined the red deposit, and in a short time he announced the discovery of a new element. Because of its frequent association with tellurium, and its many points of similarity to that element, he named it Selenium, from *σελήνη*, the moon (Annal. der Phys. u. Chem. (1818) xxix, 229).

**Occurrence.** Selenium is found usually in combination with the metals, as in the following minerals:

<i>Clausthalite</i> , $\text{PbSe}$ ,	contains.....	27-28% Se
<i>Tiemannite</i> , $\text{HgSe}$ ,	" .....	25-29% "
<i>Guanajuatite</i> , $\text{Bi}_2\text{Se}_3$ ,	" .....	24-34% "
<i>Naumannite</i> , $(\text{Ag}, \text{Pb})\text{Se}$ ,	" .....	27-30% "
<i>Berzelianite</i> , $\text{Cu}_2\text{Se}$ ,	" .....	39-40% "
<i>Lehrbachite</i> , $\text{PbSe} \cdot \text{HgSe}$ ,	" .....	24-28% "
<i>Eucairite</i> , $\text{Cu}_2\text{Se} \cdot \text{Ag}_2\text{Se}$ ,	" .....	31-32% "
<i>Zorgite</i> , <i>vid.</i> <i>Clausthalite</i> ,	" .....	29-34% "
<i>Crookesite</i> , $(\text{Cu}, \text{Tl}, \text{Ag})_2\text{Se}$ ,	" .....	30-33% "
<i>Onofrite</i> , $\text{Hg}(\text{S}, \text{Se})$ ,	" .....	4- 6% "
<i>Galenobismutite</i> , $\text{PbBi}_2\text{S}_4$ ,	" .....	0-14% "
<i>Durdenite</i> , $\text{Fe}_2(\text{TeO}_3)_3 \cdot 4\text{H}_2\text{O}$ ,	" .....	1- 2% $\text{SeO}_3$
<i>Chalcomenite</i> , $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ ,	" .....	48-49% "
<i>Tellurium</i> (native), $\text{Te}$ ,	" .....	6- 7% Se
<i>Selen-sulphur</i> , $\alpha\text{Se} \cdot \gamma\text{S}$ ,	" .....	35-66% "
<i>Selen-tellurium</i> , $3\text{Te} \cdot 2\text{Se}$ ,	" .....	29-30% "

It is found also in some volcanic lavas, and in anode muds in electrolytic copper refineries.

**Extraction.** Selenium salts may be extracted from flue-dust by the following methods:

(1) The soluble material is dissolved by treatment with water, and the selenium is extracted from the residue by aqua regia (*Berzelius, vid. Experiment 1*).

(2) The seleniferous material is digested with a solution of potassium cyanide at a temperature of  $80^\circ$ - $100^\circ$  C. until the red color has changed to gray, ( $\text{KSeCN}$ ). The selenium goes into solution and may be precipitated by hydrochloric acid (*Pettersson, Ber. Dtsch. chem. Ges. VII, 1719*).

(3) The flue-dust or mineral is fused with sodium carbonate, and the selenium is extracted with water as sodium selenide and selenite, ( $\text{Na}_2\text{Se}$ ;  $\text{Na}_2\text{SeO}_3$ ).



**The Element.** *A. Preparation.* Selenium in the elementary condition may be prepared by the action (1) of sulphur dioxide, zinc, or iron, upon selenious acid (Berzelius); (2) of hydrochloric acid upon sodium seleno-sulphite (Pettersson); (3) of potassium iodide, sodium thio-sulphate, etc., upon selenious acid.

*B. Properties.* Like sulphur, selenium is known in several allotropic modifications,\* and may be either soluble or insoluble in carbon disulphide. In soluble form selenium is a red powder which softens at  $50^{\circ}$ – $60^{\circ}$  C., is partly fluid at  $100^{\circ}$  C. and is completely fused at  $250^{\circ}$  C. After it has been melted it remains in a plastic condition for a long time and has a metallic luster. Its specific gravity is 4.2 to 4.3. From a warm solution in carbon disulphide the element separates in red, monoclinic, crystalline plates, and from a cold solution in orange-red monoclinic crystals of different type. The specific gravity of these crystalline varieties is 4.4 to 4.5. Selenium insoluble in carbon disulphide may be obtained by allowing the element to cool very slowly after it has been heated to a higher temperature than  $130^{\circ}$  C., or by allowing the oxygen of the air to act upon selenides in aqueous solution. Under these conditions the element assumes the so-called metallic form, crystallizes in steel-gray hexagonal crystals, and becomes isomorphous with tellurium. Selenium in this form is a poor conductor of electricity, but when heated to about  $200^{\circ}$  C. it becomes a good conductor. Metallic selenium melts at  $217^{\circ}$  C. without previous softening. Its specific gravity is 4.8.

Selenium boils at  $700^{\circ}$  C., yielding a dark-yellow vapor which, when condensed and cooled, assumes a form similar

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\* For discussions of these modifications, see Saunders, Jour. Phys. Chem. (1900) IV, 423; Marc, Physikalisch-chemischen Eigenschaften des metallischen Selens, pub. by Leopold Voss, Hamburg, 1907; de Coninck, Bull. Acad. roy. Belgique (1907), 365, or Chem. Zentr. (1907) II, 575; Pochettino, Atti Accad. Lincei, Roma [5] xx [1], 428.

to flowers of sulphur; this is called flowers of selenium. The element is soluble in sulphuric acid, giving a green solution, and is oxidized by nitric acid to selenious acid, ( $\text{H}_2\text{SeO}_3$ ). It combines with metals to form selenides. When heated in air or oxygen it burns with a blue flame and goes over to the dioxide, ( $\text{SeO}_2$ ). It is a poor conductor of heat and electricity.

**Compounds.\*** *A. Typical forms.* The following compounds of selenium may be considered typical:

Oxides .....	$\text{SeO}_2$	
Fluorides .....	$\text{SeF}_4$	$\text{SeF}_6? \dagger$
Chlorides. ....	$\text{Se}_2\text{Cl}_2$	$\text{SeCl}_4$
		$\text{SeCl}_3\text{Br}$
Oxychloride .....	$\text{SeOCl}_2$	
Bromides. ....	$\text{Se}_2\text{Br}_2$	$\text{SeBr}_4$
		$\text{SeClBr}_3$
Iodides. ....	$\text{Se}_2\text{I}_2$	$\text{SeI}_4$
Seleno-sulphite ....	$\text{SeSO}_3$	
Alums .....		$\overset{\text{I}}{\text{R}}_2\text{Al}_2(\text{SeO}_4)_4 + 24\text{H}_2\text{O}$
Thioselenic acid. . .		$\text{H}_2\text{SSeO}_3$
Thioseleniate. ....		$\text{K}_2\text{SSeO}_3$
Cyanides. . . . .	$(\text{CN})_2\text{Se}$	
	$(\text{CN})_2\text{Se}_3$	
	$\text{H}(\text{CN})\text{Se}$	
	$\text{K}(\text{CN})\text{Se}$	
	$\overset{\text{II}}{\text{R}}(\text{CN})\text{Se}_2$	
Nitride. ....	$\text{N}_2\text{Se}$	
Phosphides. . . . .	$\text{P}_4\text{Se}_3$	
	$\text{P}_2\text{Se}_5$	

\* Rimini, Gaz. chim. ital. xxxvii [i], 261; Pellini, Atti Accad. Lincei, Roma [5] xv [i], 629, 711; [ii], 46; xviii [ii], 211; or Review in Jour. Amer. Chem. Soc. xxix, 395.

† Ramsay, Compt. rend. cxliv, 1196; Lebeau, Compt. rend. cxlv, 190.

Selenides..... $\text{H}_2\text{Se}$   
 $\text{NiSe}$   
 $\text{Ag}_2\text{Se}$   
 $\text{Na}_2\text{Se}_2, \text{Na}_2\text{Se}_3, * \text{Na}_2\text{SeO}_3, \dagger \overset{\cdot}{\text{R}}_2\text{SeO}_4$   
 $\text{K}_2\text{Se}, \text{etc.}$   
 Acids (selenious and selenic)  $\text{H}_2\text{SeO}_3, \text{H}_2\text{SeO}_4$   
 Salts (selenites and seleniates)  $\overset{\cdot}{\text{R}}_2\text{SeO}_3, \dagger \overset{\cdot}{\text{R}}_2\text{SeO}_4$

*B. Characteristics.* The compounds of selenium, as will appear later, closely resemble those of tellurium, both in structure and in behavior toward reagents. They are, however, rather more sensitive to the action of reducing agents, and readily precipitate the red amorphous variety of the element, which tends to become black when heated. Hydrogen selenide is a gas which acts like hydrogen sulphide and hydrogen telluride, and precipitates the selenides ( $\overset{\cdot}{\text{R}}_2\text{Se}$ ). By the treatment of elementary selenium with nitric acid or aqua regia and evaporation to dryness, selenious oxide, ( $\text{SeO}_2$ ), is formed, which dissolves in water, forming selenious acid, ( $\text{H}_2\text{SeO}_3$ ). By the action of powerful oxidizing agents, such as chlorine, bromine, or potassium permanganate, selenious acid may be oxidized to selenic acid, ( $\text{H}_2\text{SeO}_4$ ), which is not reduced by sulphur dioxide. These acids form salts of the types  $\overset{\cdot}{\text{R}}_2\text{SeO}_3$  and  $\overset{\cdot}{\text{R}}_2\text{SeO}_4$ . By the action of reducing agents, such as sulphur dioxide or ferrous sulphate, red amorphous selenium may be readily precipitated from selenious acid. Two chlorides, ( $\text{Se}_2\text{Cl}_2$ ;  $\text{SeCl}_4$ ), and the corresponding bromides and iodides are known. When selenium is heated, a characteristic, penetrating odor is given off which has been variously described as like that of garlic, decayed cabbage, and putrid horse-

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\* Mathewson, Jour. Amer. Chem. Soc. XXIX, 867.

† For selenites of the rare earths see Espil, Compt. rend. CLII, 378.

radish. This odor is caused by the formation of small amounts of the hydride.

**Estimation.** *A. Gravimetric.* Selenium is generally weighed as the element, obtained by treating solutions of its compounds (1) with sulphurous acid in hydrochloric acid solution; (2) with potassium iodide in acid solution (Peirce, Amer. Jour. Sci. [4] 1, 416); (3) with hypophosphorus acid in alkaline solution (Gutbier and Rohn, Zeitsch. anorg. Chem. xxxiv, 448). Other reducing agents may be used.

*B. Volumetric.* Selenium may be determined volumetrically (1) by oxidizing selenious acid to selenic by means of standard potassium permanganate in sulphuric acid solution, using an excess of permanganate, and titrating back with oxalic acid (Gooch and Clemons, Amer. Jour. Sci. [3] L, 51); (2) by reducing selenic or selenious acid by means of potassium iodide in hydrochloric acid solution, ( $\text{SeO}_2 + 4\text{HI} = 2\text{H}_2\text{O} + \text{Se} + 2\text{I}_2$ ;  $\text{SeO}_3 + 6\text{HI} = 3\text{H}_2\text{O} + \text{Se} + 3\text{I}_2$ ), and determining by appropriate means the iodine set free (Muthmann and Schaefer, Ber. Dtsch. chem. Ges. xxvi, 1008; Gooch and Reynolds, Amer. Jour. Sci. [3] L, 254); (3) by reducing selenic acid to selenious by boiling with hydrochloric acid, ( $\text{SeO}_3 + 2\text{HCl} = \text{SeO}_2 + \text{H}_2\text{O} + \text{Cl}_2$ ), then passing the free chlorine into potassium iodide, and determining the iodine set free (Gooch and Evans, Amer. Jour. Sci. [3] L, 400); (4) by employing potassium bromide and sulphuric acid instead of hydrochloric acid in (3) (Gooch and Scoville, Amer. Jour. Sci. [3] L, 402); (5) by boiling a solution of selenious acid with sulphuric acid, a known amount of potassium iodide, and an excess of arsenic acid; the reduction of the selenious acid will decrease the reduction of arsenic acid; the quantity of arsenious acid present at the close of the action may be measured, after neutralization with potassium bicarbonate, by standard iodine (Gooch and Peirce, Amer. Jour. Sci. [4] 1, 31); (6) by the

reduction of selenious acid to elementary selenium by means of standard sodium thiosulphate solution in excess in the presence of hydrochloric acid,—the excess of thiosulphate being determined by standard iodine solution (Norris and Fay, Amer. Chem. Jour. xviii, 703; Norton, Amer. Jour. Sci. [4] vii, 287); (7) by boiling elementary selenium with ammonia and standard silver nitrate solution, acidifying with nitric acid, and determining the excess of silver nitrate by ammonium sulpho-cyanide, with ferric alum as indicator; the quantity of selenium present is calculable from the quantity of silver nitrate used, as is shown in the following equation:  $4\text{AgNO}_3 + 3\text{Se} + 3\text{H}_2\text{O} = 2\text{Ag}_2\text{Se} + \text{H}_2\text{SeO}_3 + 4\text{HNO}_3$  (Friedrich, Zeitsch. angew. Chem. xv, 852).

**Separation.** Selenium is separated, together with tellurium, from other elements by methods given under Tellurium, where the separation of these two elements from each other is also discussed.

## EXPERIMENTAL WORK ON SELENIUM.

*Experiment 1. Extraction of selenium from (1) flue-dust and (2) seleniferous residues from electrolytic refining of copper.* (1) Treat about 25 grm. of the washed flue-dust with aqua regia as long as any evidence of action is observed, and evaporate to dryness. Extract the residue with about 25 cm.<sup>3</sup> of strong common hydrochloric acid, and filter. To the filtrate add about a gram of dry ferrous sulphate, and warm gently if necessary. Filter off the red amorphous selenium.

(2) Treat about 25 grm. of the residues with strong commercial hydrochloric acid, warm as long as anything appears to dissolve, and filter. Precipitate the selenium as in (1). Save the filtrate to be examined later for tellurium.

*Experiment 2. Preparation of selenium dioxide, (SeO<sub>2</sub>).*  
To a small amount of elementary selenium add nitric acid until the oxidation is shown to be complete by the cessation of the evolution of red fumes (oxides of nitrogen). Evaporate to dryness and warm gently. The white residue is selenium dioxide. Dissolve this in a little water to form selenious acid, (H<sub>2</sub>SeO<sub>3</sub>).

*Experiment 3. Precipitation of selenites.* (a) To a little selenious acid add a few drops of a barium salt in solution. Test the action of hydrochloric acid upon the precipitate.

(b) Try the action of cupric sulphate upon a little selenious acid.

*Experiment 4. Formation of selenic acid, (H<sub>2</sub>SeO<sub>4</sub>).*  
(a) To a few cm.<sup>3</sup> of selenious acid add first a small amount of sulphuric acid and then a solution of potassium permanganate until the purple color is permanent. Bleach by the careful addition of oxalic acid.

(b) Pass chlorine gas into water in which some elementary selenium is suspended.

*Experiment 5. Reactions with selenic acid.* (a) To a solution of selenic acid formed as in 4 (b) add a little barium salt in solution. Note the precipitation of barium selenate (BaSeO<sub>4</sub>).

(b) Try the action of a solution of cupric sulphate upon a solution of selenic acid. Compare with 3 (b).

*Experiment 6. Reduction of selenic acid to selenious.*  
Add to a given volume of selenic acid half as much strong hydrochloric acid and boil to about two thirds of the total volume. Note the evolution of chlorine. Test by starch iodide paper.

*Experiment 7. Precipitation of elementary selenium.*  
Try the action of the following reducing agents upon dilute selenious acid: sulphur dioxide, hydrogen sulphide, acid sodium sulphite, potassium iodide, stannous chloride, ferrous sulphate.

*Experiment 8. Solvent action of carbon disulphide upon selenium.* To a little dry, washed, amorphous selenium add carbon disulphide. Filter, and allow the filtrate to evaporate.

*Experiment 9. Solvent action of potassium cyanide upon selenium.* To a small amount of the red amorphous selenium add a few cm.<sup>3</sup> of a dilute solution of potassium cyanide (poison!), warm gently, and filter. To the filtrate add hydrochloric acid.

*Experiment 10. Behavior of selenium when subjected to heat.* Heat a small amount of elementary selenium on a glass rod. Note the odor, and the color of the flame.

*Experiment 11. Action of strong sulphuric acid upon selenium.* To a small amount of elementary selenium add a few cm.<sup>3</sup> of strong sulphuric acid and warm. Note the green color. Allow to cool and add water. Note the precipitation of the selenium ( $\text{SeSO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_4 + \text{Se}$ ).

### TELLURIUM, Te, 127.5.\*

**Discovery.** Native tellurium, which is quite widely distributed in small quantities, was a puzzle to the early mineralogists. Because of its non-metallic properties and its metallic luster it was known as *aurum paradoxum* and *metallum problematicum*. In 1782 Müller von Reichenstein, after some careful work on this interesting substance, suggested that a peculiar metal might be present. Acting on the suggestion, Klaproth undertook an investigation, and in 1798 he demonstrated that the "metal" was not identical with any known element. He proposed the name Tellurium from *tellus, earth* (Crell Annal. (1798) 1, 91).

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\* See Lenher, Jour. Amer. Chem. Soc. xxx, 741, for a review of the work on the homogeneity of tellurium. Marckwald (Ber. Dtsch. chem. Ges. xl, 4730) claims that previous atomic weights have been defective, and gives 126.85 as the result of his work. Later (xliii, 710) by means of volumetric methods he arrives at 127.6 as the result. Browning and Flint and later Flint (Amer. Jour. Sci. [4] xxviii, 347; xxx, 209) obtained a value approaching 126.5. Harcourt and Baker (Jour. Chem. Soc. (London) xcix, 1311) reaffirm 127.5. The atomic weight of Te is evidently not settled.

identical with any known element. He proposed the name Tellurium, from *tellus*, earth (Crell Annal. (1798) 1, 91).

**Occurrence.** Tellurium occurs in combination and also, sparingly, native.

<i>Petzzite</i> , (Ag,Au) <sub>2</sub> Te,	contains..	32-35%	Te
<i>Goldschmidtite</i> , Au <sub>2</sub> AgTe <sub>6</sub> ,	" ..	59-60%	"
<i>Hessite</i> , Ag <sub>2</sub> Te,	" ..	37-44%	"
<i>Altaite</i> , PbTe,	" ..	37-38%	"
<i>Coloradoite</i> , HgTe,	" ..	38-39%	"
<i>Melonite</i> , Ni <sub>2</sub> Te <sub>3</sub> ,	" ..	73-76%	"
<i>Kalgoorlite</i> , HgAu <sub>2</sub> Ag <sub>6</sub> Te <sub>6</sub> ,	" ..	37-56%	"
<i>Sylvanite</i> , (Au,Ag)Te <sub>2</sub> ,	" ..	58-62%	"
<i>Calaverite</i> , (Au,Ag)Te <sub>2</sub> ·AuTe <sub>2</sub> ,	" ..	56-58%	"
<i>Krennerite</i> , (Au,Ag)Te <sub>2</sub> ·AuTe <sub>2</sub> ,	" ..	38-59%	"
<i>Nagyagite</i> , Au,Pb <sub>11</sub> Sb <sub>1</sub> Te <sub>7</sub> S <sub>11</sub> ,	" ..	15-31%	"
<i>Goldfieldite</i> , 5Cu <sub>2</sub> S(Sb,Bi,As) <sub>2</sub> (S,Te),	" ..	17%	"
<i>Tapalpite</i> , 3Ag <sub>2</sub> (S,Te)·Bi <sub>2</sub> (S,Te) <sub>3</sub> ?,	" ..	20-24%	"
<i>Tetradymite</i> , Bi <sub>2</sub> Te <sub>3</sub> S <sub>3</sub> ,	" ..	33-49%	"
<i>Grünlingite</i> , Bi <sub>4</sub> TeS <sub>3</sub> ,	" ..	12-13%	"
<i>Rickardite</i> , Cu <sub>2</sub> Te·2CuTe,	" ..	59-60%	"
<i>Joseite</i> , formula doubtful,	" ..	15-16%	"
<i>Wehrlite</i> , " "	" ..	29-35%	"
<i>Stützite</i> , Ag <sub>4</sub> Te?,	" ..	22-23%	"
<i>Tellurite</i> , TeO <sub>2</sub> ,	" ..	79-80%	"
<i>Montanite</i> , Bi <sub>2</sub> (OH) <sub>4</sub> TeO <sub>6</sub> ?,	" ..	24-28%	TeO <sub>2</sub>
<i>Emmonsite</i> , formula doubtful,	" ..	59-60%	Te
<i>Durdenite</i> , Fe <sub>2</sub> (TeO <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O,	" ..	47-64%	TeO <sub>2</sub>
<i>Tellurium</i> (native), Te,	" ..	93-97%	Te
<i>Selen-tellurium</i> , 3Te <sub>2</sub> Se,	" ..	70-71%	"

Tellurium is found also in residues from the electrolytic refining of copper, and in flue-dust from smelters working telluride gold ores.

**Extraction.** Tellurium may be extracted by the following methods:



(1) *From tellurium bismuth (tetradymite).* The mineral is mixed with its own weight of sodium carbonate, and oil is added until the mass has the consistency of thick paste. This is heated strongly in a well-closed crucible and then extracted with water. The extract, containing sodium sulphide and sodium telluride, ( $\text{Na}_2\text{Te}$ ), is separated by filtration from the insoluble matter and left exposed to the air. The tellurium separates as a gray powder. It may be purified by distillation (Berzelius).

(2) *From sylvanite or nagyagite.* The mineral is treated with hydrochloric acid, which dissolves the antimony, arsenic, etc. The residue is dissolved in aqua regia, the excess of acid is removed by evaporation, and the gold is precipitated by ferrous sulphate. After the removal of the gold by filtration the tellurium is precipitated by sulphur dioxide (Von Schrötter).

(3) *From flue-dust containing tellurium.* The material is treated with strong commercial hydrochloric acid (*vid.* Experiment 1).

**The Element.** *A. Preparation.* Elementary tellurium may be obtained (1) by the action of reducing agents, as sulphurous acid, stannous chloride, or hydrazine upon the salts of tellurium; and (2) by the action of air upon soluble tellurides.

*B. Properties.* Tellurium is generally considered a non-metal, though Berzelius classed it with the metals. It is known in two conditions: (1) the crystalline, in which the element has a luster like silver, and (2) the amorphous. It is unchanged in the air at ordinary temperatures, but when heated in air or oxygen it burns with a green flame, forming the dioxide ( $\text{TeO}_2$ ). It is not attacked by hydrochloric acid, but is acted upon slowly by concentrated sulphuric acid, with evolution of sulphur dioxide. It is oxidized by nitric acid and aqua regia to tellurous acid, ( $\text{H}_2\text{TeO}_3$ ), and is dissolved in hot caustic potash, forming the telluride and tellurite ( $\text{K}_2\text{Te}$ ;  $\text{K}_2\text{TeO}_3$ ). It combines with metals

to form tellurides, and some alloys. Like selenium and sulphur, it is a poor conductor of heat and electricity. Its specific gravity is from 6.1 to 6.3.

**Compounds.** *A. Typical forms.* The following are typical compounds of tellurium:

Oxides. . . . .	TeO	TeO <sub>2</sub>	TeO <sub>3</sub>
Chlorides *. . . . .	TeCl <sub>2</sub>	TeCl <sub>4</sub>	
Oxychloride. . . . .		TeOCl <sub>2</sub>	
Bromides. . . . .	TeBr <sub>2</sub>	TeBr <sub>4</sub>	
Oxybromide. . . . .		TeOBr <sub>2</sub>	
Iodides. . . . .	TeI <sub>2</sub>	TeI <sub>4</sub>	
Fluoride. . . . .		TeF <sub>4</sub>	
Double fluoride. . . . .		TeF <sub>4</sub> · KF	
Sulphite. . . . .	TeSO <sub>3</sub>		
Sulphate. . . . .		2TeO <sub>2</sub> · SO <sub>3</sub>	
Sulphides (or sulpho salts). TeS		TeS <sub>2</sub> · 3K <sub>2</sub> S	
		TeS <sub>2</sub> · Bi <sub>2</sub> S <sub>3</sub> , etc.	
Tellurides. . . . .	H <sub>2</sub> Te, CTe <sub>2</sub>		
	As <sub>2</sub> Te <sub>3</sub>		
	K <sub>2</sub> Te, etc.		
Acids (tellurous and telluric)		H <sub>2</sub> TeO <sub>3</sub>	H <sub>2</sub> TeO <sub>4</sub> †
Salts (tellurites and tellurates)		R <sub>2</sub> TeO <sub>3</sub>	R <sub>2</sub> TeO <sub>4</sub>

*B. Characteristics.* The compounds of tellurium closely resemble in general structure those of sulphur and selenium. Hydrogen telluride, (H<sub>2</sub>Te), like hydrogen sulphide, is a gaseous substance, and it precipitates metallic tellurides, (R<sub>2</sub>Te), similar to the sulphides. Two oxides, tellurous, (TeO<sub>2</sub>), and telluric, (TeO<sub>3</sub>), are well known,‡ but, unlike the corresponding oxides of sulphur, they

\* For an extended discussion of the halogen salts see Gutbier, Jour. prakt. Chem. [2] LXXXIII, 145.

† Gutbier favors the formula H<sub>4</sub>TeO<sub>6</sub>. See also Staudenmeier, Zeitsch. anorg. Chem. x, 189; Gutbier, Zeitsch. anorg. Chem. xl, 260; Faber, Zeitsch. anal. Chem. XLVI, 277.

‡ A monoxide, (TeO), also has been described.

are very sparingly soluble in water. The acids, ( $\text{H}_2\text{TeO}_3$ ;  $\text{H}_2\text{TeO}_4$ ), may be formed by acidifying solutions of the alkali salts (e.g.,  $\text{Na}_2\text{TeO}_3$  or  $\text{Na}_2\text{TeO}_2$ ) which have been formed by the action of the alkali hydroxides upon the oxides ( $\text{TeO}_2$ ;  $\text{TeO}_3$ ). Many tellurites and tellurates, ( $\text{R}_2\text{TeO}_3$ ;  $\text{R}_2\text{TeO}_4$ ), may be formed by treating the alkali tellurites or tellurates with soluble salts of the various bases. Two chlorides are known, ( $\text{TeCl}_2$ ;  $\text{TeCl}_4$ ), both of which are decomposed by water. The corresponding bromides and iodides are also known. In general, compounds of tellurium are easily reduced to the element. The reduction, however, is not accomplished quite so readily as in the case of selenium compounds.

**Estimation.\*** *A. Gravimetric.* Tellurium is usually weighed as the element, obtained by treating solutions of tellurium compounds (1) with sulphur dioxide; (2) with hydrazine sulphate in ammoniacal solution (Janasch, Ber. Dtsch. chem. Ges. xxxi, 2377); (3) with hydrazine hydrate or its salts in acid or alkaline solution (Gutbier, Ber. Dtsch. chem. Ges. xxxiv, 2724); (4) with sulphur dioxide and potassium iodide (Frericks, J. pr. Chem. [2] LXVI, 261); (5) with hypophosphorus acid (Gutbier, Zeitsch. anorg. Chem. xxxii, 295); (6) with grape-sugar in alkaline solution (Stolba, *vid.* Kastner, Zeitsch. anal. Chem. xiv, 142); (7) with acid sodium sulphite or magnesium (*vid.* Experiment 1); (8) with sulphur dioxide and hydrazine hydrochloride (Lenher, Jour. Amer. Chem. Soc. xxx, 387).

It may be weighed also as the sulphate, ( $2\text{TeO}_2 \cdot \text{SO}_3$ ), obtained by treating elementary tellurium with a mixture

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\* See Gutbier, Studien über das Tellur, pub. by Hirschfeld, Leipzig, 1902; Mac Ivor, Chem. News, LXXXVII, 17, 162.

of nitric and sulphuric acids and evaporating (Metzner, Ann. Chim. Phys. [7] xv, 203).

*B. Volumetric.* Tellurium may be estimated volumetrically (1) by the reduction of telluric acid to tellurous by means of potassium bromide in sulphuric acid solution, ( $\text{H}_2\text{TeO}_4 + 2\text{HBr} = \text{H}_2\text{TeO}_3 + \text{H}_2\text{O} + \text{Br}_2$ ), the bromine being passed into potassium iodide, and the iodine estimated by standard thiosulphate (Gooch and Howland, Amer. Jour. Sci. [3] XLVIII, 375); (2) by the reducing action of strong hydrochloric acid upon soluble tellurates, chlorine being set free and passed into potassium iodide with liberation of iodine, as above; (3) by the action of standard potassium iodide solution upon a solution of tellurous acid containing twenty-five per cent. by volume of strong sulphuric acid, ( $\text{H}_2\text{TeO}_3 + 4\text{H}_2\text{SO}_4 + 4\text{KI} = \text{TeI}_4 + 4\text{KHSO}_4 + 3\text{H}_2\text{O}$ ), tellurous iodide being precipitated as a black, curdy mass, which, when shaken, separates in such a manner that the point when precipitation ceases can easily be detected; the quantity of tellurium present is calculable from the quantity of potassium iodide used (Gooch and Morgan, Amer. Jour. Sci. [4] II, 271); (4) by the oxidation of tellurous acid by means of standard potassium permanganate in acid or alkaline solution (Norris and Fay, Amer. Chem. Jour. xx, 278; Gooch and Peters, Amer. Jour. Sci. [4] VIII, 122).

**Separation.\*** From the elements not easily reduced from their compounds to elementary form, tellurium may be separated in general by the action of sulphur dioxide in faintly acid solution; this precipitates elementary tellurium. From bismuth tellurium is separated by the action of potassium sulphide upon the precipitate thrown down from solutions by hydrogen sulphide,—the tellurium dis-

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\* See Gutbier, Studien über das Tellur.

solving. From antimony the separation may be accomplished (1) by hydrazine hydrate, the tellurium being precipitated (Gutbier, *Zeitsch. anorg. Chem.* xxxii, 260); (2) by treatment of a solution of sulpho-tellurite and sulpho-antimonite with 20% hydrochloric acid in the presence of tartaric acid, the tellurium separating out (Muthmann and Schröder, *Zeitsch. anorg. Chem.* xiv, 433). From silver tellurium is separated by hydrochloric acid, the silver being precipitated; from gold by the action of heat on the two metals, tellurium being volatilized; from mercury by the action of phosphorus acid upon a cold dilute hydrochloric acid solution of the salts, mercurous chloride being precipitated.

From selenium tellurium may be separated (1) by hydroxylamine in strong hydrochloric acid solution, the selenium being precipitated (Jannasch and Müller, *Ber. Dtsch. chem. Ges.* xxxi, 2388); (2) by sulphur dioxide in strong hydrochloric acid solution, selenium being precipitated (Keller, *Jour. Amer. Chem. Soc.* xix, 771, and xxii, 241); (3) by fusion of the elements with potassium cyanide in the presence of hydrogen, tellurium being precipitated when air is passed through a solution of the melt; (4) by the action of ferrous sulphate (*vid.* Experiment 1); (5) by the greater volatility of the bromide of selenium (Gooch and Peirce, *Amer. Jour. Sci.* [4] i, 181); (6) by the action of acetic acid on a solution of an alkali tellurite and selenite, tellurous acid being precipitated (Browning and Flint, *Amer. Jour. Sci.* [4] xxviii, 112).

## EXPERIMENTAL WORK ON TELLURIUM.

*Experiment 1. Extraction of tellurium from flue-dust, or from waste products from the electrolytic refining of copper.*

(a) Treat about 10 grm. of the material with strong commercial hydrochloric acid until nothing further dissolves,

and filter. To a small portion of the filtrate add ferrous sulphate, and warm gently. The presence of selenium will be indicated by a reddish precipitate. If selenium has thus been shown to be present, take about 5 cm.<sup>3</sup> of the original filtrate, precipitate the selenium and tellurium by acid sodium sulphite or by magnesium, wash this precipitate, return it to the remainder of the filtrate, and heat to boiling. The selenium present will be precipitated by the tellurium. Remove the selenium by filtration and set it aside. From the filtrate precipitate the tellurium by acid sodium sulphite or by magnesium (Crane, Amer. Chem. Jour. XXIII, 408).

(b) Treat the residues with ammonium hydroxide as long as anything appears to dissolve. Filter, and acidify the filtrate with acetic acid. The tellurous acid is precipitated and the selenious acid remains in solution. The tellurous acid may be further purified by dissolving the precipitate in sodium hydroxide and reprecipitating with acetic acid. Dissolve in hydrochloric acid and precipitate the element as in (a) (Browning).

*Experiment 2. Action of strong sulphuric acid upon tellurium.* To a small amount of elementary tellurium add a few cm.<sup>3</sup> of strong sulphuric acid and warm. Note the reddish-violet color. This reaction constitutes a good test for tellurium. Allow to cool and add water. (See Selenium, Experiment 11).

*Experiment 3. Preparation of tellurium dioxide, (TeO<sub>2</sub>).* To a small amount of elementary tellurium add nitric acid, evaporate to dryness, and heat gently.

*Experiment 4. Formation of an alkali tellurite, (R<sub>2</sub>TeO<sub>3</sub>).* Dissolve a little tellurium dioxide in a solution of sodium or potassium hydroxide.

*Experiment 5. Formation of telluric acid, (H<sub>2</sub>TeO<sub>4</sub>).* To a solution of an alkali tellurite add sulphuric acid until the precipitate first formed dissolves. Then add gradually

a solution of potassium permanganate until no further bleaching action is noticed.

*Experiment 6. Reduction of telluric acid.* To a solution of telluric acid prepared in the previous experiment add a little potassium bromide and sulphuric acid, and boil. Note the evolution of bromine and the reduction to tellurous acid.

*Experiment 7. Precipitation of tellurous iodide, (TeI<sub>4</sub>).* To a solution of an alkali tellurite add sulphuric acid until the precipitate first formed dissolves. Then add a few drops of a solution of potassium iodide. Note the black precipitate.

*Experiment 8. Action of potassium cyanide upon tellurium.* Fuse a small amount of elementary tellurium with potassium cyanide out of contact with the air ( $2\text{KCN} + \text{Te} = \text{K}_2\text{Te} + (\text{CN})_2$ ). Extract with water and pass air through the solution. Note the precipitation of tellurium.

*Experiment 9. Precipitation of elementary tellurium.* (a) Try the action of the following reducing agents upon separate portions of the filtrate obtained in Experiment 1 (2), Selenium, or of any acid solution containing tellurium: stannous chloride, hydrogen sulphide,\* sulphurous acid, magnesium, and acid sodium sulphite.

(b) Try the action of an alkali stannite upon a solution of an alkali tellurite.

*Experiment 10. Action of tellurium compounds before the blowpipe.* Heat on charcoal a small amount of a tellurium compound. Note the white sublimate and the green color imparted to the reducing flame.

*Experiment 11. Negative test of tellurium.* Try the action of ferrous sulphate upon an acidified solution of a tellurite.

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\* Some authors give  $\text{TeS}_2$  or  $\text{TeS} + \text{S}$  as the constitution of the precipitate by hydrogen sulphide (Snelling, Jour. Amer. Chem. Soc. xxxiv, 802).

## CHAPTER X.

### PLATINUM, Pt, 195.2.

**Discovery.** In the year 1750 William Watson presented to the Royal Society a communication from William Brownrigg in which was described a "semi-metal called Platina di Pinto" found in the Spanish West Indies. Watson stated that, so far as he knew, no previous mention had been made of this substance except by Don Antonio de Ulloa in the history of his voyage to South America, published in Madrid in 1748 (Phil. Trans. Roy. Soc. (1750) XLVI, 584). However, an earlier discovery is suggested by a statement of Scaliger in 1558, who, in combating the opinion of Cardanus, that all metals are fusible, declared that an infusible metallic substance existed in the mines of Mexico and Darien. As platinum is found in those countries, it is probably the metal referred to. The name Platinum is derived from the Spanish *platina*, the diminutive of *plata*, *silver*.

**Occurrence.** Platinum occurs alloyed with the various metals of its group—palladium, osmium, iridium, etc.—and associated with other metals, as iron, lead, copper, titanite, etc. It is found chiefly in the Ural Mountains,\* associated with chrome iron ore, magnetite, cinnabar, diamonds, and gold, but also in Brazil, Mexico, Borneo, California,†

\* See Duparc, Arch. Sc. phys. et nat. Genève [4] XXXI, 211, 322, 439, 456, 516; Priwoznic, Oesterr. Ztschr. f. Berg- u. Hüttenwesen, LX, 143, 155.

† See Mineral Resources, U. S. (1910), page 773.



Oregon, Washington, and elsewhere. The Brazilian sources have recently come into prominence, and Hussak (Zeitsch. f. Geo. XIV, 284) has described three types of ore from that country. The first is similar to the Uralian platinum in composition and associated minerals. The second contains no gold or silver, is not associated with magnetite or chromite, and often contains as much as 21% of palladium. It occurs with rutile, xenotime, and diamonds. The third type is free from iron, poor in palladium, and occurs with quartz and tourmaline. Some of the Brazilian ores contain from 73% to 83% of platinum.

Platinum comprises usually from fifty to eighty per cent. of the alloys in which it occurs. It is found combined in the mineral sperrylite,  $\text{PtAs}_2$ , which contains about fifty-three per cent. of the metal.

**Extraction.** Platinum may be extracted from its alloys by the following methods:

(1) *Fusion process.* The material is fused with sulphide of lead. The iron present combines with the sulphur. The platinum alloys with the lead, while the osmium and iridium do not. The lead-platinum alloy is separated from the mass and cupelled. The platinum is left (Deville and Debray).

(2) *Wet process.* The pulverized alloy is heated in a porcelain dish with aqua regia as long as action continues. The solution obtained is nearly neutralized with calcium hydroxide, and the iron, copper, rhodium, iridium, and part of the palladium separate. After the removal of these, the filtrate is evaporated to dryness and the residue is ignited and treated with water and hydrochloric acid. The platinum, with traces of the platinum metals, remains.

**The Element.** *A. Preparation.* As extracted from its alloys, platinum is in the elementary condition (*vid.* Extraction).

*B. Properties.* In its usual form, elementary platinum is a grayish-white metal which is very malleable and ductile, but fusible only in the oxyhydrogen blowpipe flame

or by means of the electric current. Nernst\* has determined its melting-point as  $1745^{\circ}\text{C.}$ , Guntz† has found it somewhat volatile at from  $1000^{\circ}\text{C.}$  to  $1300^{\circ}\text{C.}$ , and Moissan‡ has volatilized it in the electric furnace. At no temperature is it oxidized by water or oxygen. Quénnessen§ finds it to be slightly soluble in sulphuric acid in the presence of oxygen, and Marie|| states that it is oxidized by acid and alkaline permanganate, by persulphates, chlorates, bichromates, alkaline ferricyanide, and concentrated nitric acid. Berthelot¶ finds it to be acted upon by fuming hydrochloric acid in the presence of light and manganous chloride. It is readily soluble in aqua regia. Platinum is not acted upon by sulphur alone, but if alkalis are present with the sulphur some action takes place. It is attacked also when heated with potassium nitrate. Its specific gravity is 21.48.

Besides the ordinary form, the element platinum is known to exist in two allotropic conditions: (1) spongy platinum, obtained by the ignition of ammonium chloroplatinate, and (2) platinum-black, obtained by reducing acid solutions of platinum salts. In both of these forms platinum condenses gases on its surface.\*\*

**Compounds.** *A. Typical forms.* The following may be regarded as typical compounds of platinum:

Oxides.....	PtO	Pt <sub>3</sub> O <sub>4</sub>	PtO <sub>2</sub>	PtO <sub>3</sub>
Chlorides.....	PtCl <sub>2</sub>	PtCl <sub>3</sub>	PtCl <sub>4</sub>	
Double chlorides.....	PtCl <sub>2</sub> ·SrCl <sub>2</sub> +		PtCl <sub>4</sub> ·2AgCl, etc.	
	6H <sub>2</sub> O, etc.			
Bromides.....	PtBr <sub>2</sub>		PtBr <sub>4</sub>	
Double bromides.....	PtBr <sub>2</sub> ·2KBr, etc.		PtBr <sub>4</sub> ·SrBr <sub>2</sub> +10H <sub>2</sub> O	
Iodides.....	PtI <sub>2</sub>		PtI <sub>4</sub>	

\* Nernst, Ber. phys. Ges. iv, 48.

† Guntz, Bull. soc. chim. [3] xxxiii, 1306.

‡ Moissan, Compt. rend. cxlii, 189.

§ Quénnessen, Compt. rend. cxlii, 1341.

|| Marie, Compt. rend. cxlvi, 475.

¶ Berthelot, Compt. rend. cxxxviii, 1297.

\*\* Sieverts, Ber. Dtsch. chem. Ges. xlv, 221.

Double iodides. ....	$\text{PtI}_4 \cdot 2\text{KI}$ , etc.
Fluorides. .... $\text{PtF}_3$	$\text{PtF}_4$
Sulphides. .... $\text{PtS}$	$\text{PtS}_2$
Oxysulphide. ....	$\text{PtOS}$
Sulpho salts. ....	$\text{R}_2\text{PtS}_4$
Sulphites. ....	$\text{PtSO}_3 \cdot \overset{\text{I}}{\text{R}}_2\text{SO}_3$ ; $\text{PtSO}_3 \cdot 2\overset{\text{I}}{\text{R}}\text{Cl}$
Nitrites. ....	$\overset{\text{I}}{\text{R}}_2(\text{NO}_2)_4\text{Pt}$
Iodonitrites. ....	$\overset{\text{I}}{\text{R}}_2(\text{NO}_2)_2\overset{\text{I}}{\text{R}}\text{Pt}$
Cyanide. .... $\text{Pt}(\text{CN})_3$	
Hydro-platino-cyanic acid. .... $\text{H}_2\text{Pt}(\text{CN})_4$	
Platino-cyanides. .... $\overset{\text{I}}{\text{R}}_2\text{Pt}(\text{CN})_4$ ; $\overset{\text{II}}{\text{R}}\text{Pt}(\text{CN})_4$ , typical	
Chloroplatinic acid. ...	$\text{H}_2\text{PtCl}_6$
Chloroplatinates. ....	$\overset{\text{I}}{\text{R}}_2\text{PtCl}_6$ ; $\overset{\text{II}}{\text{R}}\text{PtCl}_6$ , typical

*B. Characteristics.* The compounds of platinum may be divided into two classes, of which the platinous and platinic oxides, ( $\text{PtO}$ ;  $\text{PtO}_2$ ), serve as types. The salts of the lower condition of oxidation are usually colorless or reddish brown; they give with hydrogen sulphide or ammonium sulphide a dark-brown precipitate of platinous sulphide, ( $\text{PtS}$ ), which is soluble in ammonium sulphide. They are decomposed at red heat, and are slowly reduced to metallic platinum when boiled with ferrous sulphate. The salts of the higher condition of oxidation have a yellow or brown color, and like the platinous salts they are decomposed at red heat. Metals in general and organic matter precipitate platinum from solutions of platinic salts. The brownish-gray platinic sulphide, ( $\text{PtS}_2$ ), is precipitated by the action of hydrogen sulphide upon a solution of chloroplatinic acid, ( $\text{H}_2\text{PtCl}_6$ ); this sulphide dissolves slowly in ammonium sulphide. Salts of potassium and ammonium act upon chloroplatinic acid precipitating the corresponding salts of that acid, ( $\overset{\text{I}}{\text{R}}_2\text{PtCl}_6$ ). When platinous chloride dissolves in potassium cyanide, platinum potas-

sium cyanide is formed,  $(K_2Pt(CN)_4 + 4H_2O)$ . Many salts of this type are known.

The platinum-ammonium compounds comprise a large number of complex salts\* of the following types:

(a) The platosamines,  $PtR_2(NH_3)_4$ ;  $PtR_2(NH_3)_3$ ;  $PtR_2(NH_3)_2$ ;  $PtR_2(NH_3)$ ; and (b) the platinamines,  $PtR_4(NH_3)_4$ ;  $PtR_4(NH_3)_3$ ;  $PtR_4(NH_3)_2$ ;  $PtR_4(NH_3)$ .

In the above formulæ R may stand for OH, Cl, Br, I, or  $NO_2$ . These compounds are formed by the action of ammonia upon the platinum salts.

Potassium iodide gives a red-brown color to very dilute solutions of platinum salts.

**Estimation.** A. *Gravimetric.* Platinum is generally weighed as the metal, obtained (1) by precipitation from solutions of compounds by means of appropriate reducing agents, such as formic acid, alcohol in alkaline solution, or magnesium (Atterberg, Chem. Ztg. xxii, 538); (2) by precipitation of the sulphide and ignition; (3) by precipitation of ammonium or potassium chloroplatinate, and decomposition by heat into the metal and the volatile or soluble alkali chloride.

B. *Volumetric.* Platinum may be estimated volumetrically by reducing the tetrachloride by means of potassium iodide,  $(PtCl_4 + 4KI = PtI_2 + I_2 + 4KCl)$ , and determining by standard sodium thiosulphate the iodine thus liberated (Peterson, Zeitsch. anorg. Chem. xix, 59).

**Separation.** From most other elements platinum may be separated by the action of reducing agents in precipitating the metal from solutions. From the metals with which it is most often found associated it may be separated by the following methods: from gold (1) by the action of ammonium chloride upon the chlorides, ammonium chloroplatinate being precipitated; (2) by the action of hydrogen dioxide and sodium hydroxide upon cold solutions,

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\* See Werner, Ber. Dtsch. chem. Ges. xl, 15; Rosenheim, Zeitsch. anorg. Chem. xliii, 34.

the gold being precipitated (Vanino and Seeman, *Ber. Dtsch. chem. Ges.* xxxii, 1968); (3) by the action of oxalic acid or ferrous salts, gold being again precipitated (Hoffmann and Krüss, *Zeitsch. anal. Chem.* xxvii, 66; Bettel, *Chem. News* lvi, 133); from silver by heating the metals with dilute sulphuric acid, silver dissolving (Steinmann, *Schweiz. Wchschr. f. Chem. u. Pharm.* xlix, 441, 453); from mercury by ignition of the metals, mercury being volatilized.

The separation of platinum from the other platinum metals is so involved with the separation of these from each other that the whole subject will be briefly considered in this place. The following methods have been suggested. (1) The ore is first treated with chlorine water, which extracts the gold, then with dilute aqua regia, which dissolves the platinum, palladium, and rhodium. From this solution the platinum is precipitated by ammonium chloride and alcohol; and from the filtrate, after neutralization with sodium carbonate, the palladium is precipitated as the cyanide by mercury cyanide. The residue from the aqua regia treatment, containing osmium, iridium, and ruthenium, is heated in air. Osmium is volatilized as the tetroxide, ruthenium sublimes as the dioxide, and iridium is left (Pirngrüber, *J. B.* (1888), 2560; Wyatt, *Eng. and Min. J.* xlv, 273). (2) A neutral or acid solution of the platinum metals, gold, and mercury, containing chlorine, is treated with dilute nitric acid and heated to boiling in a retort; osmic tetroxide distils. The solution is cooled, and shaken with ether, which withdraws the chloride of gold. After the removal of the ether and gold by means of a separating funnel the remaining solution is treated with ammonium acetate and boiled with formic acid. This treatment precipitates all the metals, which are then heated in a current of hydrogen to volatilize the mercury. The remaining metals are mixed with sodium chloride and heated with moist chlorine, and the mass is extracted with water. If there is any residue at this point it will probably

be found to be iridium and ruthenium. The solution is treated with concentrated ammonium chloride as long as any precipitate forms. This precipitate consists of the double chlorides of ammonium with platinum, iridium, and ruthenium respectively, palladium and rhodium remaining in solution. The precipitate is dissolved in warm water and treated with hydroxylamine, which reduces the iridium and ruthenium to the condition of the sesquichlorides; upon the addition of ammonium chloride platinum is precipitated as the chloroplatinate. The hydroxylamine filtrate is evaporated, the residue is heated in the presence of hydrogen and fused with potassium hydroxide and nitrate, the mass is cooled and extracted with water. Ruthenium dissolves as potassium ruthenate,  $(K_2RuO_4)$ , and iridium remains as the hydrate,  $(Ir(OH)_3)$ . The solution containing rhodium and palladium is evaporated slowly to dryness in the presence of an excess of ammonia, and the residue is dissolved in the smallest possible amount of a warm, dilute ammoniacal solution. Upon cooling, the rhodium separates as a complex chloride,  $(Rh(NH_3)_5Cl_3)$ , and the palladium remains in solution (Mylius and Dietz, *Ber. Dtsch. chem. Ges.* xxxi, 3187). (3) Gold is removed by means of dilute aqua regia. By treatment with concentrated aqua regia platinum, palladium, rhodium, ruthenium, and part of the iridium are then dissolved, while an insoluble alloy of osmium and iridium in the form of grains or plates remains. This alloy is mixed with sodium chloride and the mixture is heated in a tube with chlorine. Osmium tetroxide,  $(OsO_4)$ , distils, and sodium-iridium chloride,  $(Na_2IrCl_6)$ , remains (Wöhler, *Pogg. Annal.* xxxi, 161). To the solution of the other platinum metals in aqua regia ammonium chloride is added. The precipitate, consisting of the double salts of platinum and iridium, may by ignition be converted into iridium-bearing platinum sponge (used in the manufacture of platinum vessels). To the filtrate iron or copper is added,

which throws down the palladium, rhodium, and ruthenium as a metallic powder. From this mixture palladium and the iron or copper are dissolved by nitric acid, and the solution is then shaken with mercury, which removes the palladium (von Schneider, *Liebig Annal.* v, 264, suppl.). The mixture of rhodium and ruthenium remaining is heated with sodium chloride at low redness in a current of chlorine and the mass is extracted with water. This liquid is boiled with potassium nitrite and enough potassium carbonate to make the solution faintly alkaline. It is then evaporated to dryness and the residue is pulverized and extracted with absolute alcohol. The rhodium remains undissolved as a double nitrite of potassium and rhodium,  $(K_4Rh_2(NO_2)_{12})$ , while the ruthenium dissolves, also as a double nitrite with potassium,  $(Ru(NO_2)_6 \cdot 6KNO_2)$ .

Platinum may be separated from palladium (1) by the action of warm dilute nitric acid upon the metals, palladium dissolving; (2) by the action of a strong solution of ammonium chloride and alcohol upon the double potassium salts, the palladium salt being soluble (Cohn and Fleissner, *Ber. Dtsch. chem. Ges.* xxix, R. 876); from iridium (1) by electrolysis, the platinum being precipitated (Smith, *Amer. Chem. Jour.* xiv, 435); (2) by the action of potassium nitrite, sodium carbonate, and boiling water upon the double potassium salts, iridium being reduced to the condition of the sesquichloride and dissolved (Gibbs, *Amer. Jour. Sci.* [2] xxxiv, 347); from osmium by heating in the presence of oxidizing material, osmium tetroxide being formed and volatilized; from ruthenium by treating potassium chloroplatinate and the corresponding ruthenium salt with cold water, the ruthenium salt dissolving (Gibbs, *loc. cit.*); from rhodium (1) by the method described for the separation from ruthenium; or (2) by the action of concentrated solutions of the alkali chlorides upon these salts, the rhodium dissolving (Gibbs, *loc. cit.*).

A method of separation proposed by Leidie and Quen-

nessen (Bull. Soc. Chim. XXVII, (1902) 181, will be found outlined in Table IX, page 222.

### EXPERIMENTAL WORK ON PLATINUM.

*Experiment 1. Preparation of chloroplatinic acid from laboratory residues.* Boil the residues consisting of potassium chloroplatinate, etc., with a solution of sodium carbonate and add a little alcohol. The platinum is deposited as a black powder. Wash the powder, first with hot water, then with hot hydrochloric acid; dry it, dissolve it in aqua regia, and evaporate the liquid until the point of crystallization is reached, adding a little hydrochloric acid from time to time to remove the nitric acid, and some chlorine gas to convert any platinous acid to the platinum condition.

*Experiment 2. Precipitation of the chloroplatinates of ammonium, potassium, caesium, rubidium, and thallium, ( $R_2PtCl_6$ ).* To separate portions of a solution of chloroplatinic acid add salts of ammonium, potassium, caesium, rubidium, and thallium in solution. Note the comparative insolubility of the new compounds in water and in alcohol.

*Experiment 3. Formation of chloroplatinous acid.* To a solution of chloroplatinic acid add a little stannous chloride. Note the darkening of the color. Add a little potassium or ammonium salt in solution. Note the absence of precipitation.

*Experiment 4. Precipitation of platinum sulphide, ( $PtS_2$ ).* To a solution of chloroplatinic acid add a little hydrogen sulphide, and warm.

*Experiment 5. Precipitation of elementary platinum.* (a) To a solution of a platinum salt add sodium carbonate to alkaline reaction; add also a few drops of alcohol and boil.

(b) Try the action of oxalic acid upon a platinum salt in solution.

*Experiment 6. Action of acids upon platinum.* Try separately the action of strong hydrochloric and nitric



acids upon metallic platinum. Note the effect of a mixture of the two acids upon the metal.

*Experiment 7. Test for platinum in solution.* To a very dilute solution of a platinum salt free from chlorine add a small crystal of potassium iodide. Note the color.

### THE PLATINUM METALS (OTHER THAN PLATINUM).

Occurring almost invariably associated with platinum and usually alloyed with it are small quantities of certain rare elements which, together with platinum, comprise the group of so-called Platinum Metals. These very rare elements are the following:

Palladium, Pd, 106.7

Iridium, Ir, 193.1

Osmium, Os, 190.9

Rhodium, Rh, 102.9

Ruthenium, Ru, 101.7

**Discovery.** In 1803, in the course of the purification of a considerable quantity of crude platinum, Wollaston isolated a new metal which he named Palladium, in honor of the discovery by Olbers of the planetoid Pallas. The newly discovered element was brought to the attention of scientists anonymously through a dealer's advertisement, which offered "palladium or new silver" for sale. Much discussion as to the nature of the substance ensued, Chenevix, in particular, holding it to be an alloy of platinum and mercury. In 1805 Wollaston confessed to the discovery and naming of the metal (Phil. Trans. Roy. Soc. (1803) xciii, 290; *ibid.* (1805) xcv, 316; Nicholson's J. (1805) x, 204).

The same year that palladium was discovered, Smithson Tennant found that "the black powder which remained after the solution of platina did not, as was generally believed, consist chiefly of plumbago, but contained some unknown metallic ingredients." In 1804 he presented to the Royal Society as the result of his study a communication announcing the discovery of two new metals, Iridium, named "from the striking variety of colors which it gives while dissolving

in marine acid," and Osmium, so called because of the penetrating odor (*οσμὴ*, *odor*) of the acid obtained from the oxidation of the element when it is heated in a finely divided condition (Phil. Trans. Roy. Soc. (1804) xciv, 411).

A few days after Tennant's communication, Wollaston announced the discovery of an element in the "fluid which remains after the precipitation of platina by sal ammoniac," and suggested the name Rhodium (*ῥόδιος*, *rose-like*), "from the rose color of a dilute solution of the salts containing it" (Phil. Trans. Roy. Soc. (1804) xciv, 419).

In 1826 Osann claimed the discovery of three new elements in platinum alloys. These he named Ruthenium, Polinium, and Pluranium (Pogg. Annal. viii, 505; Amer. Jour. Sci. xvi, 384). Later he withdrew the claim. In 1844 Claus found that there was an unknown metal in the mixture of substances which had been called by Osann "ruthenium oxide," and for it he retained the name ruthenium, derived from Ruthenia, i.e. Russia, where the substance was first found (Pogg. Annal. lxiv, 192, 208; Amer. Jour. Sci. xlviii, 401).

Late in the year 1911 French (Chem. News civ, 283) announced the discovery of an element associated with the platinum metals in the dike rocks of the Nelson district in British Columbia. It had the characteristics of a noble metal and was called by him Canadium. Patterson (Chem. News cv, 84), in discussing this discovery, calls attention to the fact that palladium forms alloys with many metals, and that these alloys behave very differently from palladium and resemble elementary substances.

**Occurrence.** The very rare platinum metals, as has been already stated, are found in general in platinum-bearing material. Palladium and iridium sometimes occur native; the others always in alloys or in combination.

	% Pd	% Os	% Ir	% Rh	% Ru
Native platinum contains	0.1-3.1		traces-4.2	traces	0.2-3.4
" iridium "	0.4-0.8		27-76.8		<i>circa</i> 7
Palladium gold	5-10				
Iridosmine		17-48	40.7	0.5-12.3	0.2-6
Laurite, RuS <sub>2</sub>		<i>circa</i> 3			65
Rhodium gold				34-43	

**Extraction.** For methods of extraction of the very

**Extraction.** For methods of extraction of the very rare platinum metals see Extraction and Separation of Platinum.

**The Elements.** I. PALLADIUM. *A. Preparation.* Elementary palladium may be obtained (1) by heating the potassium double chloride with hydrogen (Roessler); (2) by heating the iodide with hydrogen; and (3) by heating the chloride or cyanide.

*B. Properties.* Palladium is a ductile, malleable, white metal which looks like platinum. It may be partially oxidized before the oxyhydrogen blowpipe. It is soluble in strong nitric, hydrochloric, and sulphuric acids, and easily soluble in aqua regia. It fuses at a lower temperature than any other of the platinum metals ( $1541^{\circ}\text{C.}$ , Nernst). In spongy form it has the power of absorbing gases.\* Its specific gravity is 11.4–11.8. It may be distinguished from the other platinum metals by the comparative ease with which it dissolves in nitric acid.

II. OSMIUM. *A. Preparation.* The element osmium may be prepared (1) by heating the amalgam in the presence of hydrogen (Berzelius); (2) by heating the sulphide in a closed coke crucible; (3) by passing the vapor of the tetroxide mixed with carbon dioxide and carbon monoxide through a heated porcelain tube; (4) by passing the vapor of the tetroxide through a heated porcelain tube containing finely divided carbon (Deville and Debray); (5) by igniting osmyldiamine chloride,  $(\text{Os}(\text{NH}_2)_4\text{O}_2\text{Cl}_2)$ , in a current of hydrogen.

*B. Properties.* Osmium, the heaviest of the platinum metals, is a bluish substance, crystals of which are harder than glass. In the compact form it is insoluble in all acids and in aqua regia, and is rendered soluble only by fusion

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\* The explosive condition of the platinum metals is explained by the property, common to these metals, of occluding hydrogen and oxygen. When heated in nitrogen or out of contact with the air they tend to lose their explosive character. Ruthenium, however, is not changed by this treatment (Cohen and Strengers, *Z. physik. Chem.* LXI, 698).

with nitrates. The amorphous modification is slowly soluble in nitric acid and in aqua regia. The specific gravity of the compact and amorphous modifications is 21.3; of the crystalline form 22.4. Osmium, like the other platinum metals, has been volatilized in the electric furnace (Moissan, *Compt. rend. cxlii*, 189); it is, however, the most refractory of the group.

III. IRIDIUM. *A. Preparation.* Metallic iridium may be obtained (1) by heating iridium-ammonium chloride, and (2) by heating iridium-potassium chloride with sodium carbonate.

*B. Properties.* Iridium, a hard, brittle metal, resembles silver and tin in appearance. The ignited form is insoluble in all acids and in aqua regia. The element is partially oxidized, however, by fusion with sodium nitrate, and the fused mass may be dissolved by boiling it with aqua regia. In spongy form iridium has the specific gravity of 15.86; after fusion the specific gravity is 21-22.

IV. RHODIUM. *A. Preparation.* Elementary rhodium may be prepared (1) by heating ammonium-rhodium sesquichloride; (2) by heating rhodium sesquichloride and sodium in a current of hydrogen; (3) by heating rhodium sulphide to a white heat; and (4) by allowing reducing agents, as formic acid, zinc, iron, alcohol in alkaline solution, hydrogen, etc., to act upon soluble salts.

*B. Properties.* Rhodium is a grayish-white metal which has the appearance of aluminum. When pure it is almost absolutely insoluble in acids and in aqua regia, but when alloyed it may be dissolved in aqua regia. It is fusible before the oxyhydrogen blowpipe, but more difficultly than platinum. It has the property of absorbing hydrogen. Of all the platinum metals rhodium is most easily attacked by chlorine. Its specific gravity is 11-12.

V. RUTHENIUM. *A. Preparation.* The element ruthenium may be obtained (1) by heating the oxide with illuminating-gas, and (2) by heating ruthenium-ammonium-mercury chloride.

**B. Properties.** Ruthenium is a hard, brittle metal, dark gray to black in color. It is almost completely insoluble in acids and in aqua regia; and osmium alone, of all the platinum metals, is more difficultly fusible. It may be slightly oxidized by fusion with caustic potash and oxidized to a greater degree by fusion with potassium nitrate. The specific gravity of the crystalline form is 12.26; of the melted form 11.4; and of the porous form 8.6.

**Compounds.** *A. Typical forms.* The following compounds of the platinum metals may be considered typical:

Oxides. ....	Pd <sub>2</sub> O				
	PdO	OsO	IrO?	RhO	RuO
	Pd <sub>2</sub> O <sub>3</sub> †	Os <sub>2</sub> O <sub>3</sub>	Ir <sub>2</sub> O <sub>3</sub>	Rh <sub>2</sub> O <sub>3</sub>	Ru <sub>2</sub> O <sub>3</sub>
	PdO <sub>2</sub>	OsO <sub>2</sub>	IrO <sub>2</sub> †	RhO <sub>2</sub>	RuO <sub>2</sub>
		(OsO <sub>3</sub> )*			(RuO <sub>3</sub> )*
		OsO <sub>4</sub>			RuO <sub>4</sub>
					(Ru <sub>2</sub> O <sub>7</sub> )*
Chlorides. ....	PdCl				
	PdCl <sub>2</sub>	OsCl <sub>2</sub>	IrCl <sub>2</sub>	RhCl <sub>2</sub>	RuCl <sub>2</sub>
		OsCl <sub>3</sub>	Ir <sub>2</sub> Cl <sub>6</sub>	Rh <sub>2</sub> Cl <sub>6</sub>	Ru <sub>2</sub> Cl <sub>6</sub>
	PdCl <sub>4</sub>	OsCl <sub>4</sub>	IrCl <sub>4</sub>		RuCl <sub>4</sub>
Bromides. ....	PdBr <sub>2</sub>				
			Ir <sub>2</sub> Br <sub>6</sub>		
	PdBr <sub>4</sub>		IrBr <sub>4</sub>		
Iodides. ....	PdI <sub>2</sub>				
			Ir <sub>2</sub> I <sub>4</sub> ?	Rh <sub>2</sub> I <sub>4</sub>	Ru <sub>2</sub> I <sub>4</sub>
			IrI <sub>4</sub>		
Sulphides. ....	Pd <sub>2</sub> S				
	PdS		IrS	RhS	
			Ir <sub>2</sub> S <sub>3</sub>	Rh <sub>2</sub> S <sub>3</sub>	Ru <sub>2</sub> S <sub>3</sub>
	PdS <sub>2</sub>	OsS <sub>2</sub>	IrS <sub>2</sub>		RuS <sub>2</sub>
					RuS <sub>3</sub>
		OsS <sub>4</sub>			
Sulphates. ....	PdSO <sub>4</sub>		Ir <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> †	Rh <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	
					Ru(SO <sub>4</sub> ) <sub>2</sub>
Sulphites. ....	PdSO <sub>3</sub> · 3Na <sub>2</sub> SO <sub>3</sub>	OsSO <sub>3</sub>			
			Ir <sub>2</sub> (SO <sub>3</sub> ) <sub>3</sub>	Rh <sub>2</sub> (SO <sub>3</sub> ) <sub>3</sub>	

\* This oxide is known only in combination.

† Wöhler, Zeitsch. anorg. Chem. LVII, 323, 398.

‡ Also alums, see Marino, Zeitsch. anorg. Chem. XLII, 213; complex oxalates, see Gialdini, Atti R. Accad. dei Lincei, Roma [5] XVI [II], 648, or Chem. Zentr. (1908) I, 107.

Sulpho salts....	$R_2Pd_2S_4$ $R_3PdS_3$			
Nitrites. ....	$Pd(NO_2)_2 \cdot 2KNO_3$ $Os(NO_2)_3^*$	$Ir_2(NO_2)_4 \cdot 6HNO_3$	$Rh_2(NO_2)_6 \cdot 6RNO_2$	$Ru_2(NO_2)_4 \cdot 6RNO_2$
Nitrates. ....	$Pd(NO_3)_2$		$Rh_2(NO_3)_6$	
Acids and corre- spond'g salts...	$H_2PdCl_4; \dagger$ $R_2PdCl_4$	$H_2OsCl_4;$ $R_2OsCl_4$	$R_2RhCl_4;$ $R_2RhCl_4 \S$	$H_2RuCl_4 \dagger$ $H_2RuCl_4$
	$H_2PdCl_4;$ $R_2PdCl_4$	$H_2OsCl_4;$ $R_2OsCl_4$	$R_2IrCl_4$	

**Characteristics.** I. PALLADIUM. The compounds of palladium resemble those of platinum, both in form and in general characteristics. As in the case of platinum, palladium combines with ammonia to form complex salts, and an oxide, (PdO), forms salts with sulphur dioxide and with nitrogen trioxide, (N<sub>2</sub>O<sub>3</sub>). In general the salts are quite easily reduced to the metal by heating; their solutions resemble a solution of platinic chloride in color. Two oxides, (PdO; PdO<sub>2</sub>), are well known, of which the lower forms the more stable compounds. These compounds give a yellowish-brown precipitate with potassium hydroxide. Solutions of palladium salts give with mercuric cyanide a yellowish-white precipitate, (Pd(CN)<sub>2</sub>); with potassium iodide a black precipitate, (PdI<sub>2</sub>), which is soluble in excess of the reagent; and with hydrogen sulphide also a black precipitate, (PdS), insoluble in ammonium sulphide.

\* See also Wintrebert, Compt. rend. CXL, 585.

† See also Gutbier, Ber. Dtsch. chem. Ges. XXXVIII, 23; XXXIX, 4134; XL, 690; Zeitsch. anorg. Chem. XLV, 166, 243; XLVII, 23.

‡ See also Howe, Jour. Amer. Chem. Soc. XXVI, 543, 942; Gutbier, Zeitsch. anorg. Chem. XLV, 166, 243; XLVII, 23; Ber. Dtsch. chem. Ges. XXXVIII, 2105, 2885.

§ See also Gutbier, Ber. Dtsch. chem. Ges. XLI, 210.

Mercuric cyanide and potassium iodide are often used as tests for palladium.

II. OSMIUM.\* Compounds of osmium are known in five degrees of oxidation. The lowest three oxides, ( $\text{OsO}$ ;  $\text{Os}_2\text{O}_3$ ;  $\text{OsO}_2$ ), are basic in character, the fourth,† ( $\text{OsO}_3$ ), is acidic, and the fifth, ( $\text{OsO}_4$ ), is also acidic, but it forms no salts. Three chlorides, ( $\text{OsCl}_2$ ;  $\text{OsCl}_3$ ;  $\text{OsCl}_4$ ), are known, corresponding to the lowest oxides. The metals sodium, potassium, and barium form salts of the type  $\text{R}_2\text{OsO}_4$ . These salts are readily decomposed, especially by acids, and form the dioxide and the tetroxide. When osmium compounds are heated in the air with oxidizing agents, or are melted with potassium nitrate, the tetroxide is obtained. It is volatile when heated, highly corrosive, and disagreeable like chlorine. It is soluble in water and is reduced by reducing agents. From potassium iodide it frees iodine, and with formic acid to which potassium hydroxide has been added it gives a violet color. With ferrous sulphate it precipitates black osmium hydroxide, ( $\text{Os}(\text{OH})_4$ ), and with hydrogen sulphide it brings down the brownish-black sulphide ( $\text{OsS}_4$ ), which is insoluble in ammonium sulphide.

III. IRIDIUM.‡ The compounds of iridium exist chiefly in three conditions of oxidation, of which the di-, tri-, and tetrachlorides may serve as types, ( $\text{IrCl}_2$ ;  $\text{Ir}_2\text{Cl}_6$ ;  $\text{IrCl}_4$ ). The iridium compounds are reduced to the metal when mixed with sodium carbonate and heated in the outer flame of a Bunsen burner. The alkali double chlorides with iridous chloride, ( $\text{IrCl}_2$ ), are in general soluble in water. Solutions of iridium salts in the lowest condition of oxidation give with potassium hydroxide a greenish precipitate,

\* See also Ruff, *Zeitsch. anorg. Chem.* LXV, 429; Gutbier, *Ber. Dtsch. chem. Ges.* XLIII, 3228, 3234; XLIV, 306, 308.

† Known only in salts.

‡ For recent work on iridium compounds see Gutbier, *Ber. Dtsch. chem. Ges.* XLII, 3905, 4770; Delépine, Vezes and Duffour, *Bull. Soc. Chim.* [4], v, 869, 872, 1084; VII, 507, 512; IX, 710, 771; *Compt. rend. CLII*, 1393, 1591.

which tends to darken when boiled. Reducing agents, as sodium formate, precipitate metallic iridium, and hydrogen sulphide precipitates from the warmed solution a brown iridium sulphide ( $\text{IrS}$ ). By means of oxidizing agents, solutions of iridescent salts may be converted into the highest condition of oxidation. From solutions of this latter type potassium hydroxide throws down a dark-brown precipitate of potassium-iridium chloride, ( $\text{IrCl}_4 \cdot 2\text{KCl}$ ), and hydrogen sulphide precipitates slowly a brown sulphide, ( $\text{Ir}_2\text{S}_3$ ). The greater number of iridium compounds are easily reduced by hydrogen on being heated. The presence of iridium may be detected by the blue color developed when the compound is heated with concentrated sulphuric acid to which ammonium nitrate has been added.

IV. RHODIUM. Although three oxides of rhodium are known and described, ( $\text{RhO}$ ;  $\text{Rh}_2\text{O}_3$ ;  $\text{RhO}_2$ ), salts of only two conditions of oxidation are generally found; of these the di- and trichlorides are types, ( $\text{RhCl}_2$ ;  $\text{Rh}_2\text{Cl}_6$ ). From solutions of rhodium salts reducing agents precipitate the metal. Hydrogen sulphide throws down from a cold solution the sulphide ( $\text{Rh}_2\text{S}_3$ ), and from a hot solution the sulphhydrate ( $\text{Rh}_2(\text{SH})_6$ ). The insolubility of the double chloride of rhodium and sodium, ( $\text{Rh}_2\text{Cl}_6 \cdot 6\text{NaCl}$ ), in water, and of the double nitrate of rhodium and potassium, ( $\text{K}_6\text{Rh}_6(\text{NO}_3)_{12}$ ), in alcohol is made use of in separating the metal from the other members of the group. Rhodium is detected in the presence of the other platinum metals by the yellow solution obtained after fusion with potassium acid sulphate and the change of color to red upon the application of hydrochloric acid.

V. RUTHENIUM. In the variety of conditions of oxidation in which they are found, the compounds of ruthenium resemble those of osmium. The lowest three oxides are basic in character, ( $\text{RuO}$ ;  $\text{Ru}_2\text{O}_3$ ;  $\text{RuO}_2$ ), and form salts of which the three chlorides, ( $\text{RuCl}_2$ ;  $\text{Ru}_2\text{Cl}_6$ ;  $\text{RuCl}_4$ ), are typical. The trioxide, ( $\text{RuO}_3$ ), is known only in combination, where



it acts as an acid and forms salts of the type  $\overset{1}{R}_2RuO_4$ . Another oxide,  $(Ru_2O_7)$ , known only in combination, forms salts represented by the formula  $\overset{1}{RRuO}_4$ . The tetroxide  $(RuO_4)$  is volatile and similar to the corresponding oxide of osmium in its chemical behavior; it has a characteristic odor. A solution of the trichloride,  $(Ru_2Cl_6)$ , throws out, when heated, a dark precipitate which is generally supposed to be an oxychloride; this precipitate is held in suspension in the liquid and gives a pronounced coloration, even in very dilute solutions. Hydrogen sulphide, acting upon solutions of ruthenium salts, precipitates a mixture of sulphides, oxysulphides, and sulphur; this mixture is brown or black, and may contain one or more of the sulphides  $Ru_2S_3$ ,  $RuS_2$ , and  $RuS_3$ .

**Estimation.** The platinum metals are weighed in the elementary condition, obtained as described under Preparation of the various metals.

Osmium may be determined volumetrically by causing potassium iodide to act upon the tetroxide in the presence of dilute sulphuric acid,  $(OsO_4 + 4KI + 2H_2SO_4 = OsO_2 + 2K_2SO_4 + 4I + 2H_2O)$ , and estimating by means of sodium thiosulphate the iodine thus liberated (Klobbie, Chem. Central-Blatt (1898) 11, 65 (abstract)). The gravimetric methods for the determination of osmium have recently been studied by Paal (Ber. Dtsch. chem. Ges. XL, 1378) and found unsatisfactory.

**Separation.** The separation of the platinum metals has been considered under Platinum. The following are additional references: Gibbs, Amer. Jour. Sci. [2] xxxi, 63; xxxiv, 341; xxxvii, 57; Forster, Zeitsch. anal. Chem. v, 117; Bunsen, Liebig Annal. cxlvi, 265; Chem. News xxi, 39; Deville and Debray, Compt. rend. lxxxvii, 441; Chem. News xxxviii, 188; Wilm, Ber. Dtsch. chem. Ges. xvi, 1524; Leidie, Compt. rend. cxxxi, 888; Bull. Soc. Chim. d. Paris [3] xxvii, 179.

## EXPERIMENTAL WORK ON THE PLATINUM METALS.

*Experiment 1. Precipitation of palladous iodide, (PdI<sub>2</sub>).* To a solution of a palladium salt add a little potassium iodide in solution.

*Experiment 2. Precipitation of palladous sulphide, (PdS).* (a) Pass hydrogen sulphide through a solution of a palladous salt.

(b) Try the action of ammonium sulphide upon a palladous salt in solution.

*Experiment 3. Precipitation of the hydroxide or basic salt.* To a solution of a palladous salt add a little sodium hydroxide or carbonate in solution.

*Experiment 4. Precipitation of palladous cyanide.* To a solution of a palladous salt add a solution of mercuric cyanide. Try the action of potassium cyanide and ammonium hydroxide upon the precipitate.

*Experiment 5. Action of ammonium chloride upon palladous and palladic chlorides.* (a) To a solution of palladous chloride add ammonium chloride.

(b) Saturate a solution of palladous chloride with chlorine and add ammonium chloride. The palladic salt (PdCl<sub>6</sub>)(NH<sub>4</sub>)<sub>2</sub> is insoluble.

*Experiment 6. Precipitation of elementary palladium.* To a solution of a palladium salt add sodium carbonate to alkaline reaction; add also a few drops of alcohol and boil.

*Experiment 7. Action of nitric acid upon palladium.* Try the action of nitric acid upon a small piece of metallic palladium.

*Experiment 8. Precipitation of osmium sulphide, (OsS<sub>4</sub>).* (a) To a solution of osmium tetroxide acidified with hydrochloric acid add a little hydrogen sulphide.

(b) Try the action of ammonium sulphide upon the tetroxide in solution.

*Experiment 9. Formation of potassium osmate,  $(K_2OsO_4)$ .* To a solution of osmium tetroxide add a solution of potassium hydroxide. Note the yellow color.

*Experiment 10. Action of reducing agents upon osmium tetroxide.* Try the action of an alkali sulphite, formic acid, and tannic acid, respectively, upon a solution of osmium tetroxide.

*Experiment 11. Action of osmium tetroxide upon hydriodic acid.* To a solution of osmium tetroxide add a little starch paste and a small crystal of potassium iodide. Acidify the solution with dilute sulphuric acid. Note the blue color, due to free iodine.

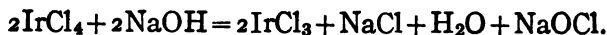
*Experiment 12. Precipitation of elementary osmium.*  
(a) To a solution of the tetroxide add stannous chloride.  
(b) Try the action of zinc and hydrochloric acid upon a solution of the tetroxide.

*Experiment 13. Odor test for osmium.* Warm a dilute solution of osmium tetroxide, or warm with nitric acid a solution of any osmium salt of the lower condition of oxidation. Note the odor.

*Experiment 14. Precipitation of iridium sulphide,  $(Ir_2S_3)$ .* Pass hydrogen sulphide through a solution of iridium tetrachloride. Try the action of ammonium sulphide upon the precipitate.

*Experiment 15. Formation of the double chlorides of iridium with ammonium and potassium,  $((NH_4)_2IrCl_6$  and  $K_2IrCl_6$ ).* To separate portions of a fairly concentrated solution of iridium tetrachloride add ammonium chloride and potassium chloride respectively.

*Experiment 16. Action of sodium hydroxide upon iridium tetrachloride.* To a solution of iridium tetrachloride add some sodium hydroxide in solution. Note the changes in color, dark red to green  $(IrCl_3)$ .



Warm the solution and note the change to azure blue.

*Experiment 17. Reduction of iridium salts.* (a) To a solution of iridium tetrachloride add oxalic acid.

(b) Try similarly the action of zinc upon an acid solution of the salt.

*Experiment 18. Action of sodium hydroxide upon iridium tetrachloride.* Add sodium hydroxide in excess to iridium tetrachloride and warm. Note the change in color. The iridium salt is said to be reduced to the trichloride by this treatment. Acidify with hydrochloric acid and add potassium chloride. Note the absence of precipitation.

*Experiment 19. Precipitation of rhodium sulphide, ( $\text{Rh}_2\text{S}_3$ ).* Pass hydrogen sulphide through a solution of sodium-rhodium chloride. Try the action of ammonium sulphide upon the sulphide precipitated.

*Experiment 20. Reduction of rhodium salts.* To an acid solution of a rhodium salt add zinc.

*Experiment 21. Formation of the double nitrite of potassium and rhodium, ( $\text{K}_3\text{Rh}(\text{NO}_2)_6$ ).* To a solution of sodium-rhodium chloride add potassium nitrite in solution and warm. Try the action of hydrochloric acid upon the precipitate.

*Experiment 22. Precipitation of rhodium hydroxide, ( $\text{Rh}(\text{OH})_3$ ).* Note the first action and the action in excess of sodium or potassium hydroxide upon a solution of sodium-rhodium chloride. Boil the solution just obtained.

*Experiment 23. Precipitation of ruthenium sulphide, ( $\text{Ru}_2\text{S}_3$ ).* (a) To a solution of ruthenium trichloride add hydrogen sulphide.

(b) Use ammonium sulphide as the precipitant.

*Experiment 24. Formation of the soluble double nitrite of ruthenium and potassium, ( $\text{K}_3\text{Ru}(\text{NO}_2)_6$ ).* To a solution

of ruthenium trichloride add a solution of potassium nitrite. Note the color. Add ammonium sulphide to the solution.

*Experiment 25. Precipitation of ruthenium hydroxide,  $(\text{Ru}(\text{OH})_3)$ .* To a solution of ruthenium trichloride add sodium or potassium hydroxide in solution.

*Experiment 26. Precipitation of metallic ruthenium.* To an acid solution of a ruthenium salt add metallic zinc.

### GOLD, Au, 197.2.

**Discovery.** Gold is probably one of the earliest known of the metals. In very ancient records frequent mention is made of its uses. As far back as 3600 B.C. in the Egyptian code of Menes a ratio of value between gold and silver (2.5:1) is mentioned. Rock carvings of Upper Egypt dating from 2500 B.C. show crude representations of the washing of gold-bearing sands in stone basins, and of the melting of the metal in simple furnaces by means of mouth blowpipes. In fact the discovery of gold dates back to the beginnings of civilization. The search for it furnished the motive of many voyages of discovery and conquest, which resulted in the extension of civilization; and from the desire to change the base metals into gold sprang the study of alchemy, from which developed the science of chemistry.

**Occurrence.** Gold occurs in nature both free and in combination. Free or native gold is found (1) as vein gold, in the quartz veins which intersect metamorphic rocks, and (2) as placer gold, generally in the form of grains or nuggets, in alluvial deposits of streams. Native gold is usually alloyed with silver, which sometimes amounts to as much as fifteen per cent. of the alloy. Iron and copper are sometimes present, and bismuth, palladium, and rhodium alloys are known.

In combination gold is found as follows:

<i>Petzite</i> , $(\text{AgAu})_2\text{Te}$ ,	contains	.....	18-24% Au
<i>Sylvanite</i> , $(\text{AuAg})\text{Te}_2$ ,	"	.....	26-29% "
<i>Goldschmidtite</i> , $\text{Au}_2\text{AgTe}_6$ ,	"	.....	31-32% "
<i>Krennerite</i> , $(\text{Au,Ag})\text{Te}_2 \cdot \text{AuTe}_2$ ,	"	.....	30-34% "
<i>Calaverite</i> , $(\text{Au,Ag Te}_2 \cdot \text{AuTe}_2$ ,	"	.....	38-42% "
<i>Kalgoorlite</i> , $\text{HgAu}_2\text{Ag}_6\text{Te}_6$ ,	"	.....	20-21% "
<i>Nagyagite</i> , $\text{Au}_2\text{Pb}_{14}\text{Sb}_8\text{Te}_7\text{S}_{17}$ ,	"	.....	5-12% "

**Extraction.** The six processes indicated below follow the principal methods that have been employed for the extraction of gold.

(1) *Washing or Hydrauliclicking.* This method is applied mainly to placer deposits. Powerful jets of water are directed upon the gold-bearing sands, causing them to pass through a series of sluices. Because of its higher specific gravity the gold is largely left behind, while the other materials are carried away.

(2) *Amalgamation (primitive).* In this process the crushed ore or the gold-bearing sand is first washed, to remove the greater part of the light, worthless material, and the remainder is rubbed with mercury in a mortar. The amalgam thus obtained is heated, whereupon the mercury is volatilized and the gold remains.

(3) *Stamp battery amalgamation.* The ore is pulverized and mixed with water, and in the form of pulp caused to pass over a series of amalgamated copper plates. Gold amalgam forms on the plates, and from time to time it is removed and cupelled.

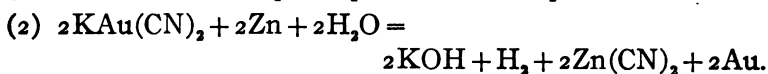
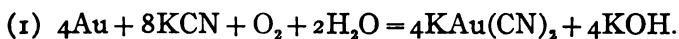
(4) *Chlorination.* (a) *Vat process.* The crushed ore is placed loosely in large vats and moistened with water. Chlorine is forced in, and the whole is allowed to stand for about twenty-four hours. The material is then leached with water until the washings give no further test for gold. The solution of gold chloride thus obtained is treated with

sulphur dioxide, to destroy the excess of chlorine, and then with hydrogen sulphide. The gold sulphide thus precipitated is decomposed with borax and the gold is melted into bullion.

(b) *Barrel process.* Into large barrels are put water and sulphuric acid, the ore, and chloride of lime. The barrels are then closed and rotated for a period varying from one hour to four hours. At the end of that time the contents are leached and the gold is extracted as described above.

The chlorination process is generally applied to low-grade ores, and these must have been roasted unless the gold occurs in them native.

(5) *Cyanide process.* The ore, ground fine, is placed in large vats, and a dilute solution (.2-5%) of potassium cyanide is forced in. After a time the solution is drawn off and passed over zinc shavings, upon which the gold is deposited as a black slime. The mixture of zinc and gold is either treated with sulphuric acid, to dissolve the zinc, or roasted with a flux of niter and carbonate of soda. The reactions which take place in the cyanide process may be represented as follows:



(6) *Smelting.* In smelting the gold ore is mixed with some other metallic ore appropriately chosen, and the mixture is subjected to intense heat. The gold alloys with the other metal, and the alloy is separated from the residue, or slag, and worked for gold. Three modifications of this important process are in common use, viz., lead, copper matte, and iron matte smelting. The process of lead-smelting is in outline as follows: The alloy obtained by heating a mixture of gold and lead ores is melted with

zinc. The gold and silver combine with the zinc and rise to the surface, leaving the lead below. The alloy of gold, silver, and zinc is then skimmed off and roasted. The zinc passes off, leaving the gold and silver, which are separated by electrolysis.

**The Element.** *A. Preparation.* As extracted from its ores gold is in the elementary condition (*vid.* Extraction).

*B. Properties.* Of a characteristic yellow color, gold is the most malleable and ductile of the metals. It is about as soft as silver. It is insoluble in the common acids, but is attacked by aqua regia, chlorine, bromine, and by potassium cyanide in the presence of oxygen. It is dissolved in many reactions where oxygen is set free, e.g. by selenic acid, and by phosphoric or sulphuric acid in the presence of telluric acid, nitric acid, lead or manganese dioxide, chromium trioxide, or potassium permanganate. It is not attacked when suspended in sulphuric acid and treated with oxygen gas (Lenher, Jour. Amer. Chem. Soc. xxvi, 550). It is somewhat soluble in hydrochloric acid in the presence of light and manganous chloride (Berthelot, Compt. rend. cxxxviii, 1297), and in thiocarbamide in the presence of oxidizing agents. (Moir, Proc. Chem. Soc. xxii, 105, 165). It has also been found to be slightly attacked by alkali sulphides and thiosulphates. Moissan has distilled it in the electric furnace; he finds that when alloys of copper or tin with gold are subjected to distillation, the copper and tin distil first (Compt. rend. cxli, 853, 977). Its melting-point is  $1037^{\circ}\text{C}$ .,—just above that of copper. Gold alloys with nearly all the metals. It is occasionally found crystallized in the cubic system. It is a good conductor of heat and electricity. Its specific gravity is 19.49.

**Compounds.** *A. Typical forms.* The following compounds of gold may be considered typical forms:



Oxides.....	$\text{Au}_2\text{O}$	$\text{Au}_2\text{O}_2$	$\text{Au}_2\text{O}_3$
Hydroxide.....			$\text{Au}(\text{OH})_3$
Aurates.....			$\text{Na}_2\text{O}_2 \cdot \text{Au}_2\text{O}_3$ , *
			$\text{BaO}_2 \cdot \text{Au}_2\text{O}_3$ , etc.
Chlorides.....	$\text{AuCl}$	$\text{Au}_2\text{Cl}_4$	$\text{AuCl}_3$
Double chlorides, many of the types			$\text{AuCl}_3 \cdot \overset{\text{I}}{\text{RCl}}$
			$\text{AuCl}_3 \cdot \overset{\text{II}}{\text{RCl}_2}$
Bromides.....	$\text{AuBr}$	$\text{Au}_2\text{Br}_4$	$\text{AuBr}_3$
Double bromides, of the type. ....			$\text{AuBr}_3 \cdot \overset{\text{I}}{\text{RBr}}$
Iodides.....	$\text{AuI}$		$\text{AuI}_3$
Double iodides, of the type. ....			$\text{AuI}_3 \cdot \overset{\text{I}}{\text{RI}}$
Sulphides.....	$\text{Au}_2\text{S}$	$\text{Au}_2\text{S}_3$	$\text{Au}_2\text{S}_3$
Double sulphides..	$\text{Au}_2\text{S} \cdot \text{Na}_2\text{S}$		$2\text{Au}_2\text{S}_3 \cdot 5\text{Ag}_2\text{S}$
			$2\text{Au}_2\text{S}_3 \cdot 3\text{MoS}_3$
			$\text{Au}_2\text{S}_3 \cdot 3\text{MoS}_4$
Sulphites (double)	$\text{Au}_2\text{SO}_3 \cdot 3\text{Na}_2\text{SO}_3 + 3\text{H}_2\text{O}$		$\text{Au}_2(\text{SO}_3)_3 \cdot 5\text{K}_2\text{SO}_3 + 5\text{H}_2\text{O}$
Sulphates.....	$\text{AuSO}_4$		$\text{Au}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4$
Nitrate.....			$\text{Au}(\text{NO}_3)_3 \cdot \text{HNO}_3$
Cyanides.....	$\text{AuCN}$		$\text{Au}(\text{CN})_3$
Double cyanides..	$\text{AuCN} \cdot \text{KCN}$		$\text{Au}(\text{CN})_3 \cdot \text{KCN}$ , etc.
Sulphocyanides..	$\text{AuCNS} \cdot \text{KCNS}$		$\text{Au}(\text{CNS})_3 \cdot \text{KCNS}$

*B. Characteristics.* The compounds of gold are known chiefly in two conditions of oxidation, of which aurous oxide,  $(\text{Au}_2\text{O})$ , and auric oxide,  $(\text{Au}_2\text{O}_3)$ , serve as types. When metallic gold is dissolved in aqua regia auric chloride is formed, a yellow crystalline salt soluble in water; when auric chloride is heated to  $180^\circ \text{C}$ . it goes over to aurous chloride, a white powder insoluble in water. The aurous salts resemble the salts of silver and of copper in the cuprous condition; the auric salts resemble those of aluminum and of iron in the ferric condition. The auric hydroxide,  $(\text{Au}(\text{OH})_3)$ , is acidic in character and unites with bases to form aurates of the type  $\overset{\text{I}}{\text{RAuO}}_2$ . Hydrogen sulphide precipitates brownish-

\* See Meyer, *Compt. rend.* CXLV, 805.

black auric sulphide, ( $\text{Au}_2\text{S}_3$  or  $\text{Au}_2\text{S}_2 + \text{S}$ ), from cold solutions of gold salts, and steel-gray aurous sulphide, ( $\text{Au}_2\text{S}$  or  $\text{Au}_2\text{S} + \text{S}$ ), from hot solutions. Salts of gold in solution are easily reduced to the metal by reducing agents.

**Estimation.\*** *A. Gravimetric.* Gold is weighed as the metal. From solutions it is precipitated by reducing agents, such as ferrous sulphate, oxalic acid, formaldehyde, and hydrogen dioxide in alkaline solution.

*B. Volumetric.* Gold may be determined volumetrically (1) by allowing potassium iodide to act upon auric chloride, ( $\text{AuCl}_3 + 3\text{KI} = 3\text{KCl} + \text{AuI} + \text{I}_2$ ), and estimating the iodine thus freed by means of thiosulphate (Peterson, *Zeitsch. anorg. Chem.* XIX, 63; Gooch and Morley, *Amer. Jour. Sci.* [4] VIII, 201; Maxson, *Amer. Jour. Sci.* [4] XVI, 155); (2) by warming a solution of auric chloride with a measured amount of arsenious acid solution which must be in excess, ( $3\text{As}_2\text{O}_3 + 4\text{AuCl}_3 + 6\text{H}_2\text{O} = 3\text{As}_2\text{O}_5 + 12\text{HCl} + 4\text{Au}$ ), and determining the excess of arsenious acid by iodine in the usual way (Rupp, *Ber. Dtsch. chem. Ges.* XXXV, 2011; Maxson, *loc. cit.*).

**Separation.** Gold and platinum fall into the analytical group of arsenic, antimony, and tin. From these they may be separated by the following process: fusion of the sulphides with sodium carbonate and niter, and removal of the arsenic by extraction with water; treatment of the insoluble residue with zinc and hydrochloric acid, which reduces the tin and antimony to the metallic condition; boiling with hydrochloric acid, which dissolves the tin; then with nitric and tartaric acids, which dissolves the antimony, leaving gold and platinum.

For the separation of gold from platinum and the platinum metals *vid.* Platinum.

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\* For the estimation of gold in telluride ores, see Hillebrand, *Bull.* 253 (1905), U. S. Geological Survey.

From selenium and tellurium gold may be separated by oxalic acid, which precipitates the gold (A. A. Noyes, Jour. Amer. Chem. Soc. XXIX, 137).

### EXPERIMENTAL WORK ON GOLD.

*Experiment 1. Extraction of gold from its ores.* (a) Digest for several hours in a beaker on a steam-bath about 100 grm. of finely ground gold ore with a dilute solution of potassium cyanide, adding water from time to time to replace the liquid evaporated. Filter, pass the filtrate several times through a funnel containing zinc shavings, until upon testing the liquid with a fresh piece of zinc no discoloration of the metal is observed. Dissolve the zinc in hydrochloric acid to remove the black deposit. Filter, dissolve the residue in aqua regia, remove the excess of acid by evaporation, and test for gold by stannous chloride, ferrous sulphate, etc.

(b) Mix in a glass-stoppered bottle about 100 grm. of finely ground "oxidized" or previously roasted ore with a little bleaching salt and enough water to give the mass the consistency of thin paste. Then add gradually enough sulphuric acid to start an evolution of chlorine. Close the bottle and shake it, to insure a thorough mixing of the contents. Allow the action to go on for several hours, agitating the mass occasionally, and taking care to have an excess of chlorine present throughout the process. Extract with water, concentrate if necessary, and test for gold in the solution. A two per cent. solution of bromine may be substituted for the materials generating chlorine.

*Experiment 2. Precipitation of the sulphide of gold, ( $\text{Au}_2\text{S}_3$  or  $\text{Au}_2\text{S}_2 + \text{S}$ ?).* Into a cold solution of auric chloride pass hydrogen sulphide. Try the action of yellow ammonium sulphide upon the precipitate.

*Experiment 3. Formation of aurous iodide, ( $\text{AuI}$ ).* To

a solution of auric chloride add a few drops of a dilute solution of potassium iodide. Note the precipitate, and the solvent action of an excess of the reagent.

*Experiment 4. Formation of ammoniu aurate, "fulminating gold,"*  $(\text{NH}_3)_2\text{Au}_2\text{O}_3$ . To a very dilute solution of a salt of gold add a little ammonium hydroxide.

CAUTION. Do not attempt to isolate the precipitate. Note that neither potassium nor sodium hydroxide gives a precipitate under similar conditions of dilution.

*Experiment 5. Formation of the "purple of Cassius."\** To a very dilute solution of a gold salt add a drop or two of dilute stannous chloride solution.

*Experiment 6. Precipitation of gold.* To separate portions of a solution of a gold salt add ferrous sulphate and oxalic acid in solution. Observe the color by transmitted light.

*Experiment 7. Solvent action of certain reagents upon gold.* Try separately upon metallic gold the action of aqua regia, chlorine or bromine water, and a dilute solution of potassium cyanide.

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\* Grünwald (Sprechsaal XLIII, 419) gives, as the composition of the "purple of Cassius," hydrogel of stannic acid colored by colloidal gold.

## CHAPTER XI.

### THE RARE GASES OF THE ATMOSPHERE.

Argon, A, 39.88

Krypton, Kr, 82.92

Helium, He, 3.99

Neon, Ne, 20.2

Xenon, X, 130.2

**Discovery.** In 1892 Lord Rayleigh, while engaged in the study of the density of elementary gases, made the important observation that the nitrogen obtained from nitric acid or ammonia was about one half of one per cent. lighter than atmospheric nitrogen (Proc. Royal Soc. LV, 340). An investigation of this difference led to the discovery two years later of the gas Argon (*ἀργός*, *inert*) by Lord Rayleigh and Professor William Ramsay (Proc. Royal Soc. LVII, 265; Amer. Chem. Jour. XVII, 225). An experiment made by Cavendish in 1785 seems also to have resulted in the separation of this gas (Phil. Trans. Roy. Soc. (1785) LXXV, 372, and (1788) LXXVIII, 271).

In the course of analytical work on uraninite undertaken by Hillebrand in 1888, a gas which he thought to be nitrogen was obtained upon the boiling of the mineral with dilute sulphuric acid (Bull. U. S. Geol. Sur. No. 78, p. 43; Amer. Jour. Sci. [3] XL, 384). In 1895 Ramsay, whose attention had been called to Hillebrand's work, and who doubted whether nitrogen could be obtained by the method de-

scribed, prepared some of the gas by Hillebrand's process from cleveite, a variety of uraninite. He then sparked the gas with oxygen over soda to remove the nitrogen. Observing very little contraction, he removed the excess of oxygen by absorption with potassium pyrogallate and examined the residual gas spectroscopically. The spectrum showed argon and hydrogen lines, and in addition a brilliant yellow line, ( $D_3$ ), coincident with the helium line of the solar chromosphere discovered by Lockyer in 1868 (Proc. Royal Soc. LVIII, 65, 81). The only previous note regarding helium as a terrestrial element is a statement by Palmieri, in 1881, that a substance ejected from Vesuvius showed the line  $D_3$  (Rend. Acc. di Napoli xx, 233); he failed to describe his treatment of the material, however, and he seems to have made no further investigation of the subject. Kayser first detected helium in the atmosphere, in 1895 (Chem. News LXXII, 89), several months after Ramsay's discovery.

The year 1898 witnessed the discovery by Ramsay and Travers of three other inert atmospheric gases. Having allowed all but one seventy-fifth of a given amount of liquid air to evaporate, and having removed the oxygen and nitrogen remaining by sparking over soda, they obtained a small amount of a gas which, while showing a feeble spectrum of argon, gave new lines as well. This newly discovered gas they named Krypton, from *κρυπτός*, *hidden* (Proc. Royal Soc. LXIII, 405).

By fractioning the residue after the evaporation of a large amount of liquid air they found evidence of a gas of greater density than krypton, and for this heavy gaseous element the name Xenon (*ξένος*, *stranger*) was chosen (Chem. News LXXVIII, 154).

The third discovery of the year by the same investigators was that of Neon (*νέος*, *new*), a gas of less density than argon. The first fraction obtained from the evaporation

of liquid air was mixed with oxygen and sparked over soda, and the excess of oxygen was removed by phosphorus. The remaining gas yielded a new and characteristic spectrum (Proc. Royal Soc. LXIII, 437).

**Occurrence.\*** Argon forms about one per cent. of the air by volume. It is found in small quantities in gases from certain mineral springs, e.g. Bath, Cauterets, Wildbad, Vöslau, the sulphur spring of Harrogate; in the gases occluded in rock salt, and in some volcanic gases (Moissan, Compt. rend. CXXXVIII, 936; CXXXV, 1085). It has been detected in some helium-bearing minerals, e.g. cleveite, bröggerite, uraninite, and malacon.

Helium, the existence of which was first observed in the sun, occurs in very small proportion in the terrestrial atmosphere. The chief sources of the gas have been certain rare minerals, among which are uraninite (pitch-blende), cleveite, monazite, fergusonite, samarskite, columbite, and malacon. It has been found also in some mineral springs, e.g. Bath, Cauterets, and Adano, near Padua.

The other gases of this group are present in the air in very minute quantities. Neon is said to constitute 0.0025% and krypton 0.00002% of the atmosphere. Traces of neon have been detected in the helium from the springs of Bath.

**Extraction.** Argon, contaminated with a greater or less percentage of the associated gases, may be extracted by the following methods:

(1) *From atmospheric nitrogen.* The nitrogen is passed over red-hot magnesium filings; a nitride is thus formed, while the argon is left uncombined (Ramsay). Heated lithium may be substituted for magnesium.

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\* See also Ramsay, Chem. News LXXXVII, 159; Nasini, Chem. Zentr. (1904) II, 77; Pesendorfer, Chem. Ztg. XXIX, 359; Rutherford, Chem. Zentr. (1905) I, 848; Kohlschütter, Ber. Dtsch. chem. Ges. XXXVIII, 1419; Prytz, Chem. Zentr. (1905) II, 1570; Ewers, Chem. Zentr. (1906) I, 1319; Moureu, Compt. rend. CXLII, 1155; CXLIII, 795; Kitchin, Jour. Chem. Soc. LXXXIX, 1568.

(2) *From air.* Induction sparks are passed through a mixture of oxygen and air contained in a vessel which is inverted over caustic potash. The oxygen and nitrogen combine and dissolve in the potassium hydroxide, leaving the argon (Rayleigh).

Helium may be obtained from its mineral sources by boiling the material with dilute sulphuric acid, or by heating *in vacuo*.

Krypton and xenon are extracted as follows: After the evaporation of a large amount of liquid air the residue is freed from oxygen and nitrogen and liquefied by the immersion of the containing vessel in liquid air. The greater part of the argon can be removed as soon as the temperature rises. By repetitions of this process the three gases can be separated from one another, krypton exercising much greater vapor pressure than xenon at the temperature of boiling air (Ramsay and Travers, Proc. Royal Soc. LXVII, 330).

Neon is obtained from the gas, largely nitrogen, that first evaporates from liquid air. This gas is liquefied, and a current of air is blown through it. The material that first evaporates is passed over red-hot copper, to remove the oxygen, and after being freed from nitrogen in the usual manner, is liquefied. By fractional distillation helium and neon are removed, and argon is left behind. By the use of liquefied hydrogen helium and neon are separated, as neon is liquefied or solidified at the temperature of boiling hydrogen, while helium remains gaseous. Several fractionations are necessary to obtain pure neon (Ramsay and Travers, Proc. Royal Soc. LXVII, 330).

**Properties.** The newly discovered constituents of the atmosphere are inert, colorless, probably monatomic gases, which have not been known to form definite compounds.\*

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\* Fisher and Schröter, Ber. Dtsch. chem. Ges. XLIII, 1435, 1442, 1454, 1465.



Argon is somewhat soluble\* in water. Its density is 19.96 and its specific heat 1.645. It solidifies at  $-191^{\circ}\text{C}.$ , melts at  $-189.5^{\circ}\text{C}.$ , and boils at  $-185^{\circ}\text{C}.$  It has been condensed to a colorless liquid (Baly and Donnan, Jour. Chem. Soc. (London) LXXXI, 914). Argon gives two distinct spectra, according to the strength of the induction current employed and the degree of exhaustion in the tube. When the pressure of the argon is 3 mm. the discharge is orange-red and the spectrum shows two particularly prominent red lines. If the pressure is further reduced, and a Leyden jar is intercalated in the circuit, the discharge becomes steel-blue and the spectrum shows a different set of lines (Crookes, Amer. Chem. Jour. xvii, 251).

Helium is slightly soluble† in water. Its density is 1.98, and it boils at about  $-268.5^{\circ}\text{C}.$  It was liquefied by Onnes (Proc. k. Akad. Wetensch. Amsterdam xi, 168; xiii, 1093) and its density in liquid form was found to be 0.122. Its spectrum is characterized by five brilliant lines,—one each in the red, yellow, blue-green, blue, and violet. Reference has already been made to the yellow line  $D_3$ .

Krypton is less volatile than argon. Its density is 41.5. Its melting-point is given as  $-169^{\circ}\text{C}.$ , and its boiling-point as  $-152^{\circ}\text{C}.$ ‡ Its spectrum§ is characterized by a bright line in the yellow and one in the green.

Xenon also is less volatile than argon, and it has a much higher boiling-point. Its density is 65.35. Its melting-point is said to be  $-140^{\circ}\text{C}.$ , and its boiling-point  $-109^{\circ}\text{C}.$ ‡ Its spectrum § is similar in character to that of argon, though the position of the lines is different.

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\* 100 volumes of water will dissolve 3.7 volumes of argon at  $20^{\circ}\text{C}.$

† 100 volumes of water will dissolve about 1.4 volumes of helium at  $20^{\circ}\text{C}.$

‡ Erdmann, Chem. Ztg. xxxi, 1075.

§ See Baly, Proc. Royal Soc. Lxxii, 84.

With the ordinary discharge the glow in the tube is blue and the spectrum shows three red and about five brilliant blue lines. With the jar and spark-gap the glow changes to green and the spectrum is characterized by four green lines (Ramsay and Travers, *Chem. News* LXXVIII, 155).

Neon is more volatile than argon. Its density is 10.1. Its melting-point is given as  $-253^{\circ}$  C., and its boiling-point as  $-243^{\circ}$  C.\* Its spectrum† is characterized by bright lines in the red, orange, and yellow, and faint lines in the blue and violet.

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\* Erdmann, *Chem. Ztg.* XXXI, 1075; Dewar, *Proc. Royal Soc.* LXVIII, 360v.

† See Baly, *Proc. Royal Soc.* LXXII, 84.

## CHAPTER XII.

### SOME TECHNICAL APPLICATIONS OF THE RARER ELEMENTS.

Lithium has found some use in the preparation of artificial mineral waters and in medicine.

Beryllium compounds are said to have been employed in the manufacture of mantles for incandescent gas lighting (Baskerville, Eng. and Min. Jour. LXXXVI, 907).

The chlorides of the rare earths have been subjected to electrolysis (Muthmann and Weiss, Liebig Ann. cccxxxi, 1; cccxxvii, 370), and have yielded a so-called "mischmetal" (45% Ce, 35% La, Pr, Nd, and 20% Sm, Er, Gd, Y), with which, as with aluminum in the Goldschmidt process, it has been found possible to reduce a number of the oxides (e.g.  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ , and  $\text{Ta}_2\text{O}_5$ ) to the elementary condition. The oxides of cerium, neodymium, praseodymium, and erbium seem to promise some application in the coloring of porcelain and glass (Waegner, Chem. Ind. (1904) xxvii, No. 12). Cerium salts have been used, like aluminum salts, as mordants in dyeing, and Barbieri (Atti R. Accad. Lincei, Roma [5] xvi [1], 395) has described their uses as catalyzing agents, their behavior being similar to that of manganese compounds. Ceric sulphate has been used in photography to reduce the density of negatives (Lumière frères and Seywetz, Chem. Ztg. Repert. (1900), 80), and both ceric nitrate and ceric sulphate have been used in making photographic paper (Lumière, Compt. rend. (1893) cxvi, 574; Chem. Ztg. Repert. (1892), 180, 235). Cerium oxalate, cerium hypophosphate, and cerium-ammonium citrate have found uses in medicine for sea-sickness.

and nervous disorders. The nitrates and salicylates of the rare-earth elements are used as antiseptic agents (Merck's Ber. (1897), 39; Kopp, Therap. Monatshefte (1901), Feb. No. 2). For purposes of oxidation ceric sulphate has been found to be a fair substitute for well-known oxidizing agents such as potassium permanganate (Zeitsch. f. Electrochem. ix, 534; Chem. Ztg. xxix, 669). Salts of yttrium, lanthanum, erbium and ytterbium have been used in disinfecting and in embalming. Praseodymium hydroxide and the acetates of praseodymium, neodymium and lanthanum have been employed as mordants, as have also mixtures of the sulphates of these earths (Baskerville and Foust). The use of the peroxides of the cerium earths in making rust-proof colors has been suggested.

Oxygen compounds of the rare earths have been employed as catalytic agents in the sulphuric acid contact process, and some of the chlorides have been used as contact material in decomposing heated hydrochloric acid gas. Cerous-ceric sulphate has found use in the manufacture of electric batteries (Baskerville, Paper on the Uses of the Rare Earths, read before the 1909-10 session of the Canadian Section of the Society of Chemical Industry). The employment of cerium alloys, pyrophoric bodies, in gas and cigar lighters is fairly familiar.

The use of thorium nitrate in the manufacture of mantles for incandescent gas lights is a well-known application of thorium, and the development of this growing and important industry has been largely responsible for the advances in rare-earth chemistry. The mantles contain about 99% of thoria and about 1% of ceria.

Thorium carbide is said to have been used in filaments for incandescent electric lamps, and the oxide in electric glowers such as the Nernst lamp. Ytria and zirconia are better for the latter purpose because they are less volatile. Bolton (Zeitsch. f. Electrochem. xvii, 816) states that

water which has been in contact with thorium seems to prolong the life of certain animal organisms, while the action upon vegetable life is injurious.

Zirconium has found application in the manufacture of the Nernst glowers, about 85% of zirconium oxide to 15% yttrium-earth oxides of the higher atomic weights being used in their manufacture. The carbide of zirconium is said to be an excellent conductor of electricity; ninety parts of it mixed with ten parts of the metal ruthenium have been made into filaments for use in the zirconium lamp (Sander, *Jour. f. Gasbel.* XLV II, 203, or *Chem. Zentr.* (1905) I, 1290; Böhm, *Chem. Ztg.* XXXI, 985, 1014, 1037, 1049). The use of zirconium nitrate as a food preservative has been mentioned (Baskerville, *Eng. and Min. Jour.* LXXXVII, 548).

Thallium has been used in the manufacture of optical glass, and is said to give a higher refractive power than lead (Lenher, *Electrochem. Ind.* (1904), II, 61).

For titanium a number of applications in the arts have been found. As ferro-titanium, an alloy containing from 30% to 55% of titanium, it is used in the manufacture of steels; it is said to add greatly to their tensile strength and elastic limit. Titanium-steel rails\* have given excellent service at the throat of the New York Central R. R. terminal yard in New York City, showing practically no wear in one year where the life of a rail had been from six to eight months. Titanium improves iron and steel by uniting, in the course of manufacture, with the oxygen and nitrogen, which pass off in slag; the formation of blow-holes is thus prevented. Cuprotitanium is employed in the manufacture of brass. The metal is also being used to a certain extent as a filament for incandescent electric lamps, and has the advantage over tungsten of a higher melting-

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\* See Dudley, *Use of Titanium in Bessemer Rails*, *Jour. Ind. and Eng. Chem.* II, 299.

point and higher electrical resistance. Rutile, titaniferous magnetite, titanium carbide and titanium suboxide are all finding use as electrodes with carbon blocks in arc lamps. Electrodes containing titanium give better distribution of color and light, higher efficiency, and lower cost of maintenance. The electrodes made of the carbide and of the suboxide are generally used as anodes. Other commercial uses of titanium are found in the employment of rutile for giving a yellow color to porcelain tile and to artificial teeth; of titanium chloride and titanous sulphate as mordants; and of titanous potassium oxalate as a mordant and yellow dye in the treatment of leather. Titanic oxide has been used as a protective paint for iron and steel, and to a limited extent as an incandescent medium for gas lights. The ferrocyanide has found employment as a substitute for Schweinfurth's green (Baskerville, Eng. and Min. Jour. LXXXVII, 10). On combustion titanium gives a brilliant light, a characteristic which has led to its use in pyrotechnics. The nitride has been suggested as a source of nitrogen for fertilizers, for the element combines readily with nitrogen, and yields ammonia on being heated with hydrogen.

Vanadium has found employment in a photographic developer, in a fertilizer for plants, in coloring material for glass, and with anilin in a black dye. Vanadyl phosphate has been found to behave physiologically like potassium permanganate (Ephraim, *Das Vanadin und seine Verbindungen*, 83). Vanadic acid ( $V_2O_5$ ) is employed in making a waterproof black ink with tannic acid, in manufacturing sulphuric acid by the contact process (Kuster, *Chem. Zentr.* (1905) 1, 328), as a substitute for gold bronze, and as a catalyzer to accelerate oxidation processes, such as the oxidation of sugar to oxalic acid, of alcohol to aldehyde, and of stannous to stannic salts (Naumann, *J. pr. Chem.* (2) LXXV, 146). Some of the oxides have been used in

ceramic decoration, and the trioxide and chloride as mordants (Baskerville, Eng. and Min. Jour. LXXXVII, 518). Probably of more importance than any of the foregoing uses of vanadium is its employment in the manufacture of steel, which gains greatly in elasticity and tensile strength by the presence of from .15% to .35% of this element, introduced as ferro-vanadium, an alloy containing about 30% of vanadium. (See pamphlets by J. Kent Smith, Amer. Vanadium Co.)

The use of the tantalum filament as a substitute for carbon was an interesting step in the development of incandescent electric lighting. The tantalum lamp produces a light of one candle-power for every two watts of electrical energy, as against three and one-tenth watts required by the ordinary carbon lamp. The tantalum filament, however, seems to have been superseded to a great extent by tungsten. (Mineral Resources U. S. 1908-1910.) The hardness of tantalum and its resistance to chemical action have suggested its use in pens; and pure or alloyed with iron, silicon, boron, aluminum, tin, or titanium it has been used in watch springs, clock movements, anvils, and tools for cutting (Baskerville, Eng. and Min. Jour. LXXXVI, 1100). It has been employed in the manufacture of burnishers for use in dentistry.

The element niobium is said to have found some use in the manufacture of filaments for incandescent lamps, and some of its compounds in the preparation of mantles for gas lighting (Baskerville, Eng. and Min. Jour. LXXXVI, 960).

Molybdenum alloyed with iron has been used in the manufacture of steel, but its employment in this industry seems to be on the decline. Molybdenum wire is said to have found some use as a support for tungsten filaments (Mineral Resources U. S. 1908-1910). Ammonium molybdate is an important reagent in the analysis of

phosphates. It has also been applied in fire-proofing and as a germicide and disinfectant. Sodium molybdate is employed in coloring pottery and porcelain, and in dyeing silks and woollens. Molybdenum tannate with logwood extracts finds use in dyeing leather, and "molybdenum indigo" ( $\text{Mo}_2\text{O}_7$ ) is a useful but expensive pigment for india rubber (Baskerville, Eng. and Min. Jour. LXXXVI, 1055).

Doubtless the most interesting use of tungsten at present is that of its metallic filament in electric lighting. With its melting-point of about  $3000^\circ \text{C.}$ , this metal makes a lamp which gives one candle-power of light for every one and twenty-five hundredths watts of electrical energy, as against two watts required by the tantalum lamp; and which has a life of one thousand or more hours, or about twice as long as that of the carbon and tantalum lamps. A disadvantage of the tungsten lamp, at first, was the extreme fragility of the filament. Recent improvements in manufacture, however, have made feasible not only the safe shipment of tungsten lamps, but the equipment of railroad trains and automobiles with them. Siemens and Halske, A.-G., of Berlin, Germany, have taken out patents on a process for increasing the ductility of tungsten by adding 8%-20% of nickel. The high melting-point of the element has suggested its possible use in the manufacture of crucibles (Mineral Resources U. S. 1908-1910.) Certain salts are used in weighting silks. Sodium tungstate is employed in fireproofing draperies, as a mordant in dyeing, and with potassium tungstate in the production of magenta and saffron bronzes. Tungstic oxide is used as an oil and water color (Baskerville, Eng. and Min. Jour. LXXXVII, 203). Calcium tungstate, on account of its fluorescence, is used in the Roentgen ray apparatus; lead tungstate has been substituted for white lead in paints. Compounds of tungsten have been employed in coloring



glass and porcelain. The alloy with aluminum is used in French automobile construction, and the alloy with aluminum and copper in the blades of propellers. Alloyed in small percentages with steel, tungsten is used for the following purposes: (a) to toughen armor plate; (b) to stiffen car springs; (c) to increase the permanency of magnets; (d) to increase the vibratory response in sounding-plates and wires for musical instruments; (e) to prevent projectiles and high-speed tools from losing their temper when hot (Van Wegenen, *Chem. Engineer* IV, 217). Hale (*Eng. and Min. Jour.* LXXXVII, 813) states that tungsten steel is a poor shock-resisting steel, but has great crushing strength.

Uranium salts are used in the production of certain velvety-black glazes for pottery, and of greenish-yellow iridescent glass. The possible use of uranium in steels has been suggested, but this element seems not to be as satisfactory for the purpose as vanadium or tungsten. The employment of the carbide in filaments for electric lighting has also been mentioned (Baskerville, *Eng. and Min. Jour.* LXXXVII, 257). Uranium acetate has been used in medicine as a precipitant of proteids.

Elementary selenium has the peculiar property of being a fairly good conductor of electricity in the light,\* while in the dark it is practically a non-conductor. This property has been made of service in the construction of electrical apparatus for automatically lighting and extinguishing gas-buoys, for exploding torpedoes by a ray of light, for telephoning along a ray of light, for transmitting sounds and photographs to a distance by telegraph or telephone wire, and for measuring the quantity of Roentgen rays in therapeutic applications (Hess, *Mineral Resources U.S.* 1906-1910). Selenium cells have been constructed for measuring the

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\* Ries (*Physikal, Ztschr.* XII, 480) discusses reasons for this property.

intensity of light (Huels, Bull. Univ. Wisconsin, Madison, No. 157, 419). Selenium compounds are finding important applications in the manufacture of red enamel ware, in the enameling of steel, and in the production of red glass for use in railroad signals (Jour. Ind. and Eng. Chem. iv, 539). Sodium selenite has been employed to show the reducing power of bacteria (Merck's Index, 1907).

Tellurium has shown certain peculiar behavior toward electricity which has suggested that some electrical uses may be found for the element (Hess, Mineral Resources U. S. (1908), 719).

The element platinum is finding increasing use in jewelry, and continues to be important in the manufacture of chemical apparatus. Recently 2000 kilos were reported as having been used in one year in the production of pins for artificial teeth. Its application in the sulphuric acid contact process is most important.

Iridium, alloyed with osmium, is employed for compass-bearings and for tips of gold pens. Its alloy with platinum is used in the manufacture of laboratory apparatus and for standard weights and measures. The black oxide finds use in china-painting.

Osmium has long been employed as a stain in microscopic work,\* and more recently as a filament for incandescent lamps (Jour. f. Gasbel. XLIV, 101; XLVIII, 184; Chem. Zentr. (1907) II, 433).

Palladium, because of its hardness and unalterability in air, is used for graduated surfaces of fine apparatus. It has also found use in alloys for dental work, and on account of its comparatively low fusing-point it is employed in soldering the other platinum metals.

Rhodium alloyed with platinum (10% of Rh) has been used in making thermo-elements for high-temperature work.

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\* Schultze, Zeitsch. f. wiss. Mikroskop. xxvii, 465.

Ruthenium, as has been already stated, has been mixed with zirconium carbide for use in the filament of the zirconium lamp.

The uses of gold in coinage, in jewelry, and in dentistry need no description.

## CHAPTER XIII.

### THE QUALITATIVE SEPARATION OF THE RARER ELEMENTS.

The following schemes of separation will give some idea of the problems of qualitative analysis in the presence of some of the rarer elements. None of the schemes given considers the possible presence of all of these elements.

Tables I and III include original methods which have given fairly satisfactory results in the hands of the author's classes.

Tables II, VI, and VIII, together with a considerable part of the material contained in the accompanying directions and notes were prepared from the publications of A. A. Noyes and his associates, to whom the author acknowledges his indebtedness. No attempt has been made here to take up the study of the separation methods in detail, nor to indicate the processes used for the separation of the commoner elements from one another when the rarer elements are not involved. All these processes are fully discussed in the original papers, to which reference is made.

Tables IV and V offer processes worked out by James, but rather beyond the scope of any but advanced students. They have been added, however, without explanatory notes, merely to show the best methods of attack on the complicated problem of rare earth analysis; and references to the original papers have been furnished.

In Table VII the method suggested by Böhm has been put into diagrammatic form. In this scheme no attempt was made by Böhm to give anything further than a process for the separation of the more important rare earths from other elements and from one another. To make the table more complete, however, methods for the separation of the other rare elements mentioned have been supplied.

## I

### THE ALKALI GROUP.

Before taking up the analysis as outlined in Table I, the student is advised to review by means of the following experiments the reactions of the elements involved, and to put the results into tabular form. Use solutions of the chlorides of Li, Na, K, Rb, and Cs, respectively. Perform the experiments upon separate portions of these solutions. (1) Addition of solution of  $\text{H}_2\text{PtCl}_6$ ; (2) of  $\text{Na}_3\text{Co}(\text{NO}_2)_6$ ; (3) of  $\text{NH}_4\text{F} + \text{NH}_4\text{OH}$  to alkaline reaction; (4) of  $\text{PbCl}_2 + \text{Cl}_2$ ; (5) of  $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$  and warm; (6) evaporation with  $\text{Al}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4$ ; (7) dehydration of chlorides and carbonates with amyl alcohol; (8) review of flame and spectroscopic tests.

TABLE I.

The alkalis present as chlorides.\*

Dissolve about 1-5 grms. of the mixed salts in water, and dehydrate with amyl alcohol.

R	F
Na, K, Rb, Cs. Dissolve in a few drops of water, boil with $\text{Ag}_2\text{CO}_3$ , and filter. Evaporate to dryness, and boil with amyl alcohol.	Li. Confirm by spectroscopy.]
R	F
Dissolve in about 5 cm.* of water, acidify with HCl, add $\text{H}_2\text{PtCl}_6$ † and ethyl alcohol to 50% of the total volume.	Cs. Confirm (1) by spectroscopy, (2) by precipitation with a solution of $\text{PbO}_2$ in HCl. See page 15.
P	F
K, Rb, as chloroplatinates. Decompose by gentle ignition or $\text{H}_2\text{S}$ , remove Pt, add a little aluminum sulphate and crystallize. $\text{RbAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ crystallizes before $\text{KAlSO}_4 + 12\text{H}_2\text{O}$ . See page 12. Confirm by spectroscopy.	Na. Add a few drops of a solution of $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$ and warm.

\* If the alkalis are present as salts of mixed volatile acids, they may be converted to the sulphates by evaporation with  $\text{H}_2\text{SO}_4$  to the fuming-point. The sulphates may be converted to the carbonates by treating with an excess of  $\text{Ba}(\text{OH})_2$  in solid form, filtering off the  $\text{BaSO}_4$  and insoluble excess of  $\text{Ba}(\text{OH})_2$ , and removing the  $\text{Ba}(\text{OH})_2$  in solution as insoluble  $\text{BaCO}_3$  by passing  $\text{CO}_2$  and boiling. The alkalis are left in solution as carbonates, from which form they may easily be converted to any salt desired.

† A fair separation of Rb and K may be accomplished by precipitating with  $\text{H}_2\text{PtCl}_6$  without the addition of alcohol.  $\text{Rb}_2\text{PtCl}_6$  is much less soluble than  $\text{K}_2\text{PtCl}_6$ . See page 12.

NOTE. Remove alcohol by evaporation or ignition before making confirmatory tests for Cs and Na.

## II

## THE ALUMINUM AND IRON GROUP.

Before beginning work upon this analysis the student should review the reactions of the elements involved. The common elements Fe and Al are included in the experiments suggested, as they are typical members of their respective subdivisions.

Upon separate solutions of the following salts:  $\text{FeCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{TiCl}_3$ ,  $\text{ZrCl}_4$ ,  $\text{AlCl}_3$ ,  $\text{BeCl}_2$ ,  $\text{UO}_2\text{Cl}_2$  and  $\text{NaVO}_3$  perform the following experiments, and record the results in tabular form: (1) Add  $\text{HCl} + \text{H}_2\text{S}$ ; (2) add  $\text{NH}_4\text{OH} + (\text{NH}_4)_2\text{S}$  to the product of (1); (3) add  $\text{NaOH} + \text{Na}_2\text{O}_2$  to an  $\text{HCl}$  solution of any precipitate obtained in (2); (4) add  $\text{NH}_4\text{OH}$  to portions of the original solutions; (5) warm solutions of the Al, V, Be, and U salts in a closed bottle with  $\text{NaHCO}_3$ ; (6) shake separate portions of  $\text{HCl}$  (1.12) solutions of the hydroxides of  $\text{Fe}^{\text{III}}$ ,  $\text{Ti}$ ,  $\text{Zr}$  and  $\text{Tl}^{\text{III}}$  with ether in a separation funnel, and test the resulting layers; (7) dehydrate the chlorides of  $\text{Fe}^{\text{III}}$ ,  $\text{Ti}$ ,  $\text{Zr}$  and  $\text{Tl}^{\text{III}}$  with amyl alcohol; (8) add  $\text{NaHPO}_4$  to solutions of Ti and Zr salts in presence and absence of  $\text{H}_2\text{O}_2$ ; (9) add  $\text{Na}_2\text{SO}_3$  followed by  $\text{KI}$  to solutions of  $\text{Tl}^{\text{III}}$  and  $\text{Fe}^{\text{III}}$  salts; (10) add strong  $\text{HCl}$  to concentrated solutions of chlorides of Be and Al; (11) dehydrate concentrated solutions of the nitrates of Be and Al with amyl alcohol; (12) add  $\text{NaHPO}_4$  to solutions of U and V salts.

## DIRECTIONS AND NOTES FOR Al AND Fe GROUP.

Boil out  $\text{H}_2\text{S}$  if present. Add  $\text{NH}_4\text{OH}$  in distinct but not large excess; note precipitate; pass  $\text{H}_2\text{S}$  to saturation, warm, filter, wash with dilute  $(\text{NH}_4)_2\text{S}$  and then with water. Avoid the use of  $(\text{NH}_4)_2\text{S}$  as precipitant because of its solvent action upon Ni. Transfer the precipitate with 5-20  $\text{cm}^3$  of  $\text{HCl}$  (1.12). Stir before warming, then boil a few minutes. If a black residue remains add a few drops of  $\text{HNO}_3$ .

(1.42) and boil. Evaporate nearly to dryness with  $\text{HNO}_3$  to remove  $\text{HCl}$ . Dilute to 10–20  $\text{cm}^3$ ,\* make alkaline with  $\text{NaOH}$ , add water to double the volume of the liquid. Add gradually 0.5–3 grms. of  $\text{Na}_2\text{O}_2$  with stirring. Add 5  $\text{cm}^3$  of 10%  $\text{Na}_2\text{CO}_3$ , unless it is known that the alkali earths are absent; boil to remove excess of  $\text{Na}_2\text{O}_2$ . Cool, add equal volume of water, and filter.

$\text{HCl}$  is added before  $\text{HNO}_3$  to avoid oxidizing effect of  $\text{HNO}_3$  and formation of  $\text{H}_2\text{SO}_4$ , which in turn interferes with test for  $\text{CrO}_4$  by Ba and Pb salts.  $\text{HNO}_3$  is necessary to dissolve sulphides of Ni, Co, and V.  $\text{HCl}$  must be removed by evaporation, because chlorides interfere with test for  $\text{CrO}_4$  by Pb. If  $(\text{NH}_4)_2\text{S}$  precipitate is allowed to stand for some time before treating it with acid, or if the mixture is heated a long time after precipitation,  $\text{ZrO}(\text{OH})_2$  and  $\text{TiO}(\text{OH})_2$  tend to remain undissolved after treatment with acids, because of partial dehydration. These compounds may be dissolved by  $\text{HF}$  in Pt dish, and  $\text{HF}$  removed by evaporation with  $\text{HNO}_3$  or  $\text{HCl}$ .  $\text{Na}_2\text{O}_2$  oxidizes Fe, Mn, Co, Ni, <sup>I</sup>Tl, Cr, and U. U goes into solution as peruranate.

Al GROUP.—To the filtrate from the  $\text{Na}_2\text{O}_2$  precipitate add  $\text{HNO}_3$  (1.20), keeping the solution cool until it reacts faintly acid. Dilute the solution to 100  $\text{cm}^3$ ; transfer to a flask, and place a funnel in the mouth of the flask. Add  $\text{NaHCO}_3$  until the mixture, on shaking, no longer turns litmus red at once, and add about 1–5 grms. of solid  $\text{NaHCO}_3$ . Warm 20–30 minutes on a water bath. Cool and filter.

Alkaline solution is kept cool during neutralization to avoid reduction of <sup>VI</sup>Cr to <sup>III</sup>Cr salt. Care must be taken to keep strictly to the directions about the use of  $\text{NaHCO}_3$ . Stronger solutions dissolve Be.

Dissolve the precipitate in dilute  $\text{HCl}$  and add  $\text{NH}_4\text{OH}$  in moderate excess. Heat to boiling, filter, and wash thoroughly. Dissolve the precipitate in dilute  $\text{HNO}_3$ , evaporate to a few  $\text{cm}^3$ , and dehydrate with amyl alcohol. Be dissolves. To the filtrate from the  $\text{NaHCO}_3$  treatment add  $\text{HNO}_3$  (1.20) until the solution is distinctly acid but not in excess. If the solution is colorless, Cr is absent, and the treatment with Pb salt and  $\text{H}_2\text{S}$  may be omitted. If Cr is absent neutralize the acid with  $\text{NH}_4\text{OH}$ , add acetic acid, 1–2 grms. of  $(\text{NH}_4)_2\text{SO}_4$ , 2 grms. of  $\text{Na}_2\text{HPO}_4$ , and heat to boiling. Filter, and wash with a solution

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\* If rare earths are to be tested for, treat this solution, only faintly acid with  $\text{HNO}_3$ , with  $\text{NaF}$  to complete precipitation of fluorides of rare earths. Filter and reserve precipitate for rare earth analysis. Continue with filtrate as directed above.



of  $(\text{NH}_4)_2\text{SO}_4$ . Dissolve in dilute  $\text{HCl}$ , evaporate, add  $\text{NaCl}$  and  $\text{K}_4\text{FeC}_6\text{N}_4$ . Dark red = U.

Neutralize the filtrate from the  $\text{NaHPO}_4$  filtrate with  $\text{NH}_4\text{OH}$  in slight excess and saturate with  $\text{H}_2\text{S}$ . Pink or violet = V.

**Fe GROUP.**—Dissolve the  $\text{Na}_2\text{O}_2$  precipitate in 5–30  $\text{cm}^3$  of dilute  $\text{HCl}$ , warm, filter off paper, etc., and evaporate to about 2  $\text{cm}^3$ . Add about 5  $\text{cm}^3$  of strong  $\text{HNO}_3$ ; and boil to remove  $\text{HCl}$ . Add 5–20  $\text{cm}^3$  of strong  $\text{HNO}_3$  and boil, adding 0.5 gm. of  $\text{KClO}_3$ . Filter off the  $\text{MnO}_2$  on glass wool or asbestos.

$\text{HCl}$  is used rather than  $\text{HNO}_3$  because  $\text{HNO}_3$  does not dissolve  $\text{MnO}_2$  readily.  $\text{HCl}$  is removed by  $\text{HNO}_3$  because  $\text{HCl}$  dissolves  $\text{MnO}_2$ .

If phosphates are absent (if present use acetate method) add  $\text{NH}_4\text{OH}$  in distinct excess to the filtrate from the  $\text{MnO}_2$ , filter, wash, and remove the water present, by suction if necessary. Dissolve in  $\text{HCl}$  (1.12), being careful to use this strength of acid. Add to the cold solution an equal volume of ether, and shake in a separation funnel. Draw off the layers, and repeat this operation with the water layer until the ether layer remains colorless.

The extraction of  $\text{FeCl}_3$  is most complete when the acid is 1.12. The absence of  $\text{FeCl}_3$  from the ether layer may be shown by lack of color. The water layer may have yellow color due to  $\text{TiO}_2$ . Phosphoric acid does not interfere with the separation.

Evaporate the ether extract on a water or steam bath, dissolve the residue in a little dilute  $\text{H}_2\text{SO}_4$  and water. To the cold solution add a little  $\text{KI}$  solution and  $\text{Na}_2\text{SO}_3$  until iodine color has disappeared. Yellow  $\text{TlI}$  indicates  $\text{Tl}$ . Confirm by green flame. Evaporate the water layer on a steam bath until the ether is expelled. Add dilute  $\text{H}_2\text{SO}_4$  and evaporate to the fuming-point. Cool, add 5  $\text{cm}^3$  of water, 10  $\text{cm}^3$  of 3%  $\text{H}_2\text{O}_2$ , and 10  $\text{cm}^3$  of 10%  $\text{Na}_2\text{HPO}_4$  solution. Orange-red coloration =  $\text{Ti}$ ; white, flocky precipitate,  $\text{ZrOHPO}_4$  =  $\text{Zr}$ . Allow the mixture to stand about an hour before filtering. If filtrate is still colored, add powdered  $\text{Na}_2\text{SO}_3$  until the color bleaches. Precipitate, white, flocky  $\text{TiOHPO}_4$  =  $\text{Ti}$ .

The precipitation of the phosphate of  $\text{Zr}$  is slow, so that some time should be allowed for it to form. The oxidation with  $\text{H}_2\text{O}_2$  is necessary to keep the  $\text{Ti}$  from precipitating with the  $\text{Zr}$ . If rare earths are present they should be removed by  $\text{HF}$  before testing for  $\text{Ti}$  and  $\text{Zr}$ .

TABLE II.\*

To a solution containing members of this group add  $\text{NH}_4\text{OH}$  and pass  $\text{H}_2\text{S}$ .

<p>Al, Cr, Be, Ti, Zr, V (partly), as hydroxides. Fe, Zn, Co, Ni, Mn, U, Ti, as sulphides. Dissolve in <math>\text{HCl} + \text{HNO}_3</math>, evaporate, add <math>\text{NaOH}</math>, <math>\text{Na}_2\text{O}_2</math>, and <math>\text{Na}_2\text{CO}_3</math>.</p>		<p>Alkalies and alkali earths (in the absence of phosphoric acid).</p>	
<p>Pf (Fe Group.)</p>		<p>Pf (Al Group.)</p>	
<p>Mn, Fe, Co, Ni, Ti, Zr, Zn (partly), as hydroxides. Dissolve in <math>\text{HCl}</math>, evaporate, heat with <math>\text{HNO}_3</math> and <math>\text{KClO}_4</math>.</p>		<p>Zn, Cr, Al, V, Be, U, in solution as sodium salts. Add <math>\text{HNO}_3</math>, dilute, add <math>\text{NaHCO}_3</math>, and heat in a closed bottle.</p>	
<p>Pf Mn</p>		<p>Pf Zn, Al, Be, as hydroxides or carbonates. Dissolve in <math>\text{HCl}</math>, add <math>\text{NH}_4\text{OH}</math>.</p>	
<p>Pf Fe, Ti, Zr, Ti, as hydroxides. Dissolve in <math>\text{HCl}</math> (1.12) and shake with ether.</p>		<p>Pf Be, Al, ash hydroxides.† Dissolve in <math>\text{HCl}</math>, add ether, and saturate with <math>\text{HCl}</math> (gas).</p>	
<p>Pf Ether layer. Evaporate, dissolve in dilute <math>\text{H}_2\text{SO}_4</math>, add <math>\text{KI}</math> and <math>\text{Na}_2\text{SO}_3</math>.</p>		<p>Pf Zn</p>	
<p>Pf Yellow.</p>		<p>Pf PbCrO<sub>4</sub>. Pass <math>\text{H}_2\text{S}</math>.</p>	
<p>Pf Yellow.</p>		<p>Pf Add bromine, boil, neutralize, add <math>\text{HC}_2\text{H}_3\text{O}_2</math>, and <math>\text{Na}_2\text{HPO}_4</math>.</p>	
<p>Pf Yellow.</p>		<p>Pf Add <math>\text{NH}_4\text{OH}</math> and saturate with <math>\text{H}_2\text{S}</math>. Red solution indicates V.</p>	

\* Before using this table the student should carefully study the original article (Noyes, Bray and Spear, Jour. Amer. Chem. Soc., xxx, 481).  
† Test for  $\text{H}_2\text{PO}_4^-$  and if present modify treatment.  
‡ A satisfactory qualitative separation of Be and Al may be accomplished by dehydrating the nitrates with amyl alcohol. The  $\text{Be}(\text{NO}_3)_2$  dissolves. (Browning and Kuzirian).

## III

## THE RARE EARTH GROUP.

Before taking up the analysis indicated in Table III the student is directed to review the reactions of the elements involved, and to put the results in tabular form.

Upon separate solutions of the following salts,  $\text{Y}(\text{NO}_3)_3$ ,  $\text{Ce}(\text{NO}_3)_3$ ,  $\text{Pr}(\text{NO}_3)_3$ ,  $\text{Nd}(\text{NO}_3)_3$ ,  $\text{La}(\text{NO}_3)_3$ ,  $\text{Ce}(\text{NO}_3)_4$  and  $\text{Th}(\text{NO}_3)_4$ , try the action of the following reagents in solution: (1)  $\text{NaOH}$ ,  $\text{NH}_4\text{OH}$ , or  $\text{KOH}$ ; (2)  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$ ; (3)  $(\text{NH}_4)_2\text{CO}_3$ ; (4)  $\text{H}_2\text{C}_2\text{O}_4$ ; (5)  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ; (6)  $\text{NaF}$ ; (7)  $\text{Na}_2\text{S}_2\text{O}_3$ , and warm; (8)  $\text{H}_2\text{O}_2$ ; (9)  $\text{K}_4\text{FeC}_6\text{N}_6$ ; (10)  $\text{Na}_2\text{HPO}_4$ ; (11)  $\text{KIO}_3$ ; (12)  $\text{K}_2\text{CrO}_4$ ; (13) sebacic acid; (14)  $\text{Cl}$  or  $\text{Br}$  upon the suspended hydroxides; (15)  $\text{K}_2\text{SO}_4$  to saturation. Try also the action of acetic and dilute hydrochloric acids upon the precipitates formed in (1), (2), (4), (10), (11), and (12), and the action of  $\text{H}_2\text{O}_2$  upon the hydroxides.

TABLE III.

If rare earths are to be tested for, treat the hydrochloric acid solution of the Fe and Al group precipitate with  $\text{NaF}$ .\* This precipitates the fluorides of the rare and possibly the alkali earths. The precipitate should be thoroughly washed, and evaporated with  $\text{H}_2\text{SO}_4$  to decompose the fluorides. This process removes the alkali earths as insoluble sulphates. The solution containing the sulphates of the rare earths, with excess of  $\text{H}_2\text{SO}_4$  removed, is treated with  $\text{Na}_2\text{S}_2\text{O}_3$ , and warmed.

P	F
$\text{Th}(\text{S}_2\text{O}_3)_2$ .	Ce and Y earths.
Dissolve in $\text{HCl}$ .	Saturate with $\text{Na}_2\text{SO}_4$ .
Precipitate with $\text{H}_2\text{C}_2\text{O}_4$ , wash thoroughly.	P
Dissolve in $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , acidify with $\text{HCl}$ .	$x\text{Ce}_2(\text{SO}_4)_3 \cdot y\text{Na}_2\text{SO}_4$ .
P confirms Th.	Decompose with $\text{NaOH}$ ,† and add $\text{H}_2\text{O}_2$ . Reddish yellow = Ce.‡
	Add $\text{NH}_4\text{OH}$ ; white P, which dissolves in acid, and is pptd. by $(\text{NH}_4)_2\text{C}_2\text{O}_4 = \text{Y}$ .

\* Noyes, Bray, and Spear evaporate the  $\text{HCl}$  solution of the Al and Fe group to dryness and treat with  $\text{HF}$ . They state that the fluorides of Al and Cr are somewhat insoluble in  $\text{HF}$ , and that Ti and Zr, if present, tend to retain  $\text{HF}$ .

† The double sulphates may be conveniently decomposed by fusion with an equal weight of pure charcoal (sugar carbon) in a porcelain crucible. The residue after fusion, consisting mainly of sulphides, dissolves readily in dilute  $\text{HCl}$  (Browning and Blumenthal, Amer. Jour. Sci. [4] xxxii, 164).

‡ If the presence of other Ce earths is suspected, they may be removed from Ce by treating the hydroxides suspended in a solution of  $\text{NaOH}$  with  $\text{Cl}$  or  $\text{Br}$ . These earths dissolve, leaving  $\text{CeO}_2$ .

TABLE IV.\*

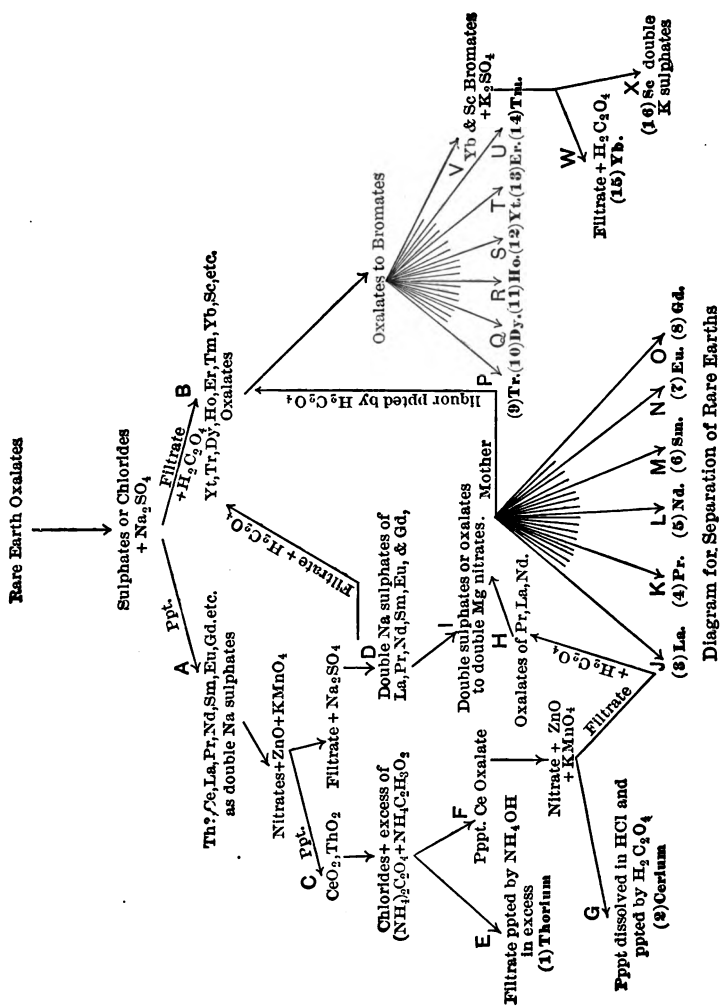


Diagram for Separation of Rare Earths

[By permission of the Journal of the American Chemical Society.]

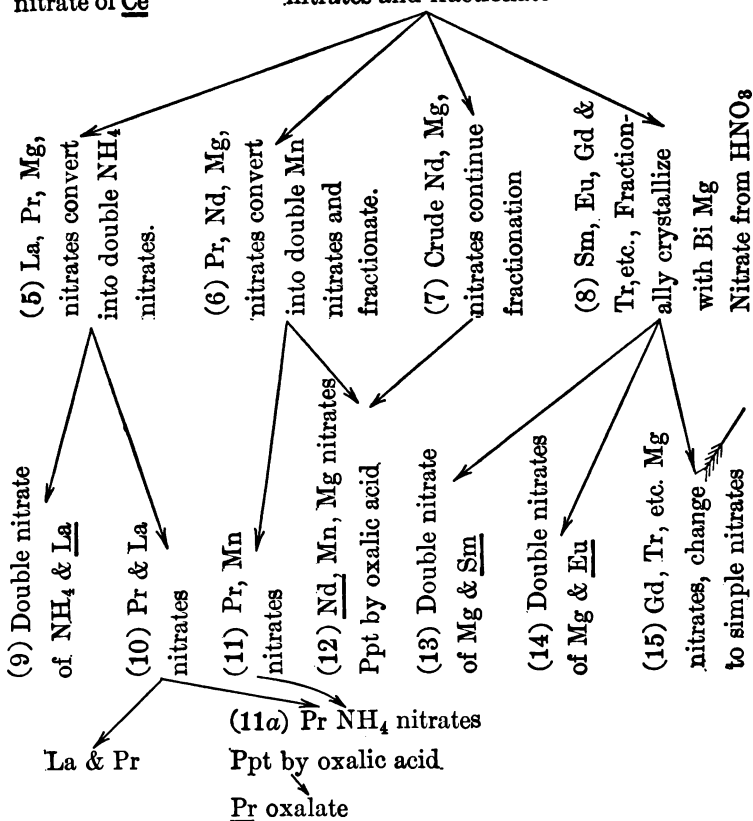
\* This diagram, published by C. James in 1908 (Jour. Amer. Chem. Soc., xxx, 979) will serve to give a satisfactory idea of the best methods in use, at the time of its publication, for the detailed separation of the rare earths. For details reference is made to the original paper.

# CHLORIDES OF La, Ce,

(1) Ppt, La, Pr, Nd, Sm, Eu, Gd & traces of Tr, Dy, etc, double Na sulfates. Convert into nitrates and boil with  $\text{KBrO}_3$  and  $\text{CaCO}_3$ .

(3) Ppt basic nitrate of Ce

(4) Solution pptd by oxalic acid  
Transform oxalates into double Mg nitrates and fractionate



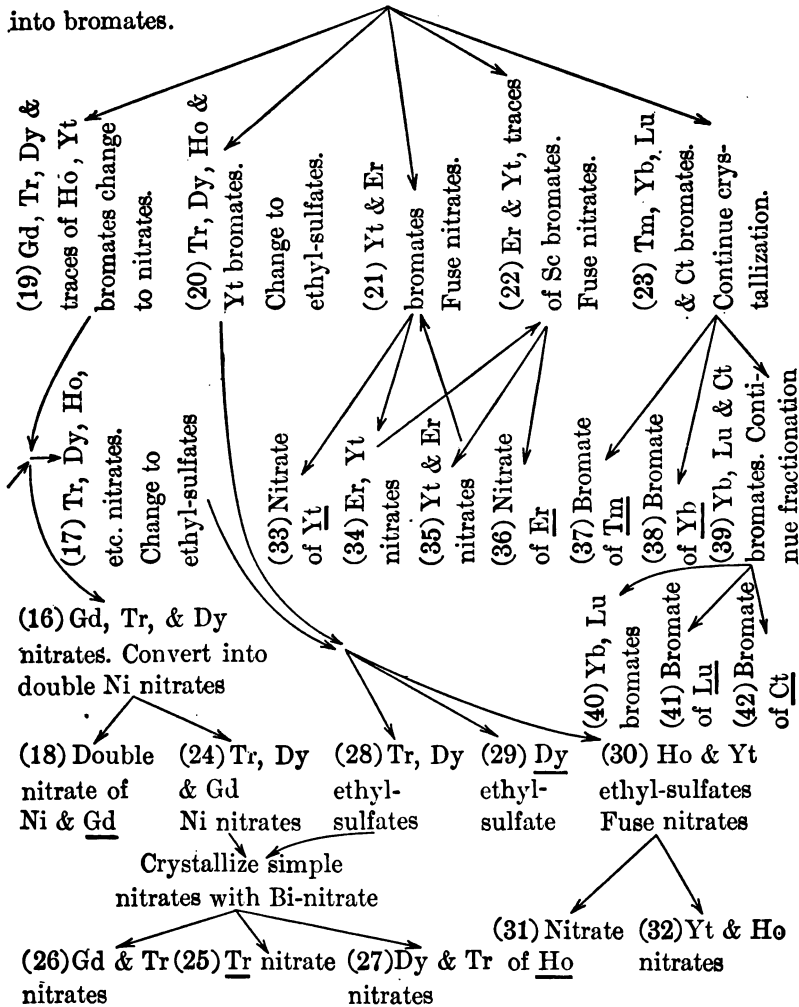
\* This diagram, published by James in 1912 (Jour. Amer. Chem. Soc., xxxiv, 757) of Th and Zr. For descriptive details see original article.

[By permission of the Journal of

V.\*

**Pr, ETC., + Na<sub>2</sub>SO<sub>4</sub>**

(2) Solution ppt'd by oxalic acid Tr, Dy, Ho, Yt, Er, Tm, Yb, Lu & Ct with traces of Sc, Gd, Eu, & Sm oxalates Converted into bromates.



brings the problem of rare earth separation to date. It assumes the previous removal

the American Chemical Society and the Author.]

## IV.

## SILVER, COPPER AND TIN GROUP.

Before taking up the analysis outlined in Table VI, the student is directed to review the reactions of the rare elements involved. Lead, mercury, and arsenic are included for purposes of comparison. Taking separate portions of solutions of the following compounds,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{TiNO}_3$ ,  $\text{HgCl}_2$ ,  $\text{AuCl}_3$ ,  $\text{H}_2\text{PtCl}_6$ ,  $\text{H}_2\text{SeO}_3$ ,  $\text{H}_2\text{TeO}_3$ ,  $\text{K}_3\text{AsO}_3$ , and  $(\text{NH}_4)_2\text{MoO}_4$ , make the following experiments, and record the results in tabular form: (1) Add  $\text{HCl}$ ; (2) add hot water to any precipitate formed in (1); (3) add  $\text{H}_2\text{SO}_4$  to solutions of  $\text{Pb}$  and  $\text{Tl}$ ; (4) add  $\text{KI}$  to solutions of  $\text{Pb}$  and  $\text{Tl}$ ; (5) add  $\text{H}_2\text{S}$  to separate solutions of all the salts mentioned above; (6) add  $(\text{NH}_4)_2\text{S}$  to all sulphides precipitated in (5); (7) add  $\text{HNO}_3(1:3)$  to the sulphides of  $\text{Hg}$ ,  $\text{Pb}$ ,  $\text{Pt}$ , and  $\text{Au}$ ; (8) add  $\text{Br}$  water and  $\text{KCl}$  to the sulphides of  $\text{Hg}$ ,  $\text{Pt}$ , and  $\text{Au}$ ; (9) add  $\text{NaOH}$  and  $\text{H}_2\text{C}_2\text{O}_4$  to solutions of  $\text{Au}$  and  $\text{Hg}$ ; (10) acidify with  $\text{HCl}$  the sulpho salts of  $\text{As}$ ,  $\text{Pt}$ ,  $\text{Au}$ ,  $\text{Se}$ ,  $\text{Te}$ , and  $\text{Mo}$ ; (11) add  $\text{HCl}$ , then  $\text{KClO}_3$  to the sulphides of  $\text{As}$ ,  $\text{Pt}$ ,  $\text{Au}$ ,  $\text{Se}$ ,  $\text{Te}$ , and  $\text{Mo}$ ; (12) add  $\text{HCl}$ , then  $\text{Na}_2\text{SO}_3$  to solutions of  $\text{Se}$ ,  $\text{Te}$ , and  $\text{Mo}$ ; (13) add  $\text{KI}$  to solutions of  $\text{Te}$  and  $\text{Mo}$ .

## DIRECTIONS AND NOTES FOR Ag, Cu, AND Sn GROUP.

Add 4  $\text{cm}^3$  of  $\text{HCl}$  (dilute). Filter, wash with cold water (about 10  $\text{cm}^3$ ). Test the filtrate for traces of  $\text{Tl}$  and  $\text{Pb}$ .

$\text{PbCl}_2$  and  $\text{TlCl}$  are somewhat soluble in cold water (20-40 mgs. of  $\text{PbCl}_2$  and 5-15 mgs. of  $\text{TlCl}$  may remain in solution). The solubility of these chlorides in water is decreased by the presence of  $\text{HCl}$  in moderate amount.

**Ag GROUP.**—Treat the precipitate of  $\text{AgCl}$ ,  $\text{PbCl}_2$ , and  $\text{TlCl}$  with 10  $\text{cm}^3$  of boiling water, pouring it back and forth several times. Treat the hot water extract containing  $\text{Pb}$  and  $\text{Tl}$  with one-fifth its volume

of strong  $\text{H}_2\text{SO}_4$ , allow to cool and stand a few minutes. Wash with dilute  $\text{H}_2\text{SO}_4$ , since  $\text{PbSO}_4$  is slightly soluble in water. To the solution containing  $\text{Tl}$  add 2-3  $\text{cm}^3$  of 1%  $\text{KI}$ . If free  $\text{I}$  appears, add  $\text{H}_2\text{SO}_4$ . Yellow  $\text{TlCl}$  indicates  $\text{Tl}$ .

$\text{Tl}$  is more insoluble than  $\text{TlCl}$ . Its solubility is decreased by  $\text{KI}$ .  $\text{Tl}$  is oxidized to  $\text{Tl}^{\text{III}}$  by  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ , and aqua regia.  $\text{Tl}^{\text{III}}$  is reduced by  $\text{H}_2\text{SO}_3$ .  $\text{Tl}^{\text{I}}$  is slightly oxidized by  $\text{HNO}_3$ .  $\text{Tl}^{\text{III}}$  is not precipitated by  $\text{HCl}$ .

**Cu AND Sn GROUP.**—Before adding  $\text{H}_2\text{S}$  see that the volume of the solution is about 40  $\text{cm}^3$  of which 4  $\text{cm}^3$  is  $\text{HCl}$  (1 : 12). Heat the solution to boiling, and saturate with  $\text{H}_2\text{S}$ . Use a flask fitted with stopper and delivery tubes, so that gentle pressure can be obtained. After saturating, add equal volume of water, cool, saturate again.

$\text{H}_2\text{S}$  is passed at boiling temperature for  $\text{As}$ ,  $\text{Pt}$ , and  $\text{Mo}$ . Pressure is used to precipitate  $\text{Pt}$  metals and  $\text{Mo}$ . The small volume of liquid, 40  $\text{cm}^3$ , is to keep  $\text{Ti}$ ,  $\text{Bi}$ , and  $\text{Sb}$  from precipitating as hydroxides or basic salts, and to precipitate  $\text{As}$  more readily. The final dilution and cooling is to precipitate all of the  $\text{Cd}$ ,  $\text{Pb}$ , and  $\text{Sn}$ .

Digest precipitate with 10-20  $\text{cm}^3$  of  $(\text{NH}_4)_2\text{S}$ , add equal volume of water, filter, and wash.

$\text{MoS}_2$  dissolves in moderate amount of  $(\text{NH}_4)_2\text{S}$  and gives a deep orange-red color to solution. Its presence in  $\text{Cu}$  Group does not interfere.  $\text{PtS}_2$  is not completely dissolved by  $(\text{NH}_4)_2\text{S}$ .

**Cu GROUP.**—Add 10-20  $\text{cm}^3$   $\text{HNO}_3$  (one-third strength), boil gently a few minutes. Dissolve residue in 10-40  $\text{cm}^3$  of saturated bromine water. Cover dish and warm 5-10 minutes. Expel excess of bromine, add 0.5 gm.  $\text{KCl}$ , 1-2  $\text{cm}^3$   $\text{HCl}$  (1 : 12). Evaporate until  $\text{KCl}$  crystallizes, cool, add water until  $\text{KCl}$  dissolves. Filter, wash with  $\text{KCl}$ . Yellow  $\text{K}_2\text{PtCl}_6 = \text{Pt}$ . Dissolve in hot water, test by  $\text{KI}$ . Make filtrate alkaline with 10%  $\text{NaOH}$ , add saturated solution of  $\text{H}_2\text{C}_2\text{O}_4$  to acidity, dilute to 15  $\text{cm}^3$  and warm 10-15 minutes on steam bath. Purple or dark yellow =  $\text{Au}$ .

$\text{K}_2\text{PtCl}_6$  is much less soluble in  $\text{KCl}$  than in water. Color with  $\text{KI}$  due to  $\text{K}_2\text{PtI}_6$ .  $\text{Au}$  is precipitated readily by  $\text{H}_2\text{C}_2\text{O}_4$  only when solution is slightly acid and hot. Precipitation takes place slowly.

**Sn GROUP.**—Dilute the  $(\text{NH}_4)_2\text{S}$  solution, acidify with  $\text{HCl}$  and warm gently; drain as dry as possible on a filter and warm with  $\text{HCl}$  (1 : 20), which removes  $\text{Sn}$  and  $\text{Sb}$ . Warm with 5-10  $\text{cm}^3$   $\text{HCl}$  (1 : 12), add a little  $\text{KClO}_3$ , evaporate to 2  $\text{cm}^3$ , or until  $\text{KCl}$  crystallizes out (see test for  $\text{Pt}$ ,  $\text{Cu}$  Group). After removing  $\text{Pt}$ , remove  $\text{As}$  by  $\text{NH}_4\text{OH}$  and  $\text{MgCl}_2$  mixture. To the filtrate add some  $\text{H}_2\text{C}_2\text{O}_4$ , boil out  $\text{NH}_3$ ,



make slightly acid with  $\text{H}_2\text{C}_2\text{O}_4$ , and test for Au as in Cu Group. Evaporate filtrate from Au nearly to dryness, add  $10 \text{ cm.}^3$  HCl, and if KCl separates filter it off. Add 0.2 gm.  $\text{Na}_2\text{SO}_3$  and allow to stand a few minutes, adding more  $\text{NaSO}_3$  if odor of  $\text{SO}_2$  is not distinct. Red  $\text{Se}=\text{Se}$ .

Reaction more delicate in cold because red, not black,  $\text{Se}$  forms.  $\text{Te}$  is reduced by  $\text{Na}_2\text{SO}_3$  if HCl is much more dilute than 1 : 12.

Dilute filtrate from  $\text{Se}$ , add equal volume of water, a little KI solution, and  $\text{Na}_2\text{SO}_3$ . Black  $\text{Te}=\text{Te}$ . Filter after a few minutes.

KI is added because  $\text{TeI}_4$  is more readily reduced by  $\text{SO}_2$  than is  $\text{TeCl}_4$ . Molybdic acid is slowly reduced by HI with liberation of I; therefore  $\text{Te}$  should be filtered off before confused with this color.

Boil filtrate from  $\text{Te}$  until  $\text{SO}_2$  is expelled. Add a little 10% KSCN and some Zn. Red color = Mo.

The  $\text{SO}_2$  is boiled out to avoid precipitation of S by Zn. Long continued action of Zn will cause bleaching of red color.

TABLE VI.\*

## SILVER, COPPER, AND TIN GROUPS.

Add HCl F PbCl <sub>2</sub> (partly) TiCl (partly) Hg <sub>2</sub> Cl <sub>2</sub> AgCl Treat with hot water.		Add H <sub>2</sub> S. F Copper and Tin Groups. Add (NH <sub>4</sub> ) <sub>2</sub> S.		Iron and Aluminum Groups, etc., see Table II.	
R Hg <sub>2</sub> Cl <sub>2</sub> AgCl Add H <sub>2</sub> SO <sub>4</sub>		R Hg, Pb, Bi, Cu, Cd, Sn, Pt, Au, Mo†, as sulphides. Treat with HNO <sub>3</sub> .		R As, Sn, Sb, Pt, Au, Se, Te, Mo, as sulpho salts. Acidify with HCl and warm the precipitate with HCl, 1.20.	
P PbSO <sub>4</sub> Add KI. P-TII		R Hg, Sn, Pt, Au, as sulphides. Add bromine solution, filter off SnO <sub>2</sub> , add KCl, and evaporate.		R As, Pt, Au, Se, Te, Mo, as sulphides. Dissolve in HCl and KClO <sub>3</sub> , and evaporate to small volume.	
P K <sub>2</sub> PtCl <sub>6</sub>		F Add NaOH and H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> and heat.		F Add NH <sub>4</sub> OH, NH <sub>4</sub> Cl, and MgCl <sub>2</sub> .	
P Au		F Hg		F Heat with H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .	
		F Evaporate, add strong HCl, and Na <sub>2</sub> SO <sub>4</sub> .		F Add water and KI.	
		F Boil out SO <sub>2</sub> , add KSCN and Zn.		F Red Mo(SCN) <sub>4</sub> .	

\* Before making use of this table the student should carefully study the original article (Noyes and Bray, Jour. Amer. Chem. Soc., **xxix**, 137).

† Amount present negligible.

TABLE VII.\*

Add HCl.		F	
Ag, Hg, Pb, Ti, as chlorides. H <sub>2</sub> SiO <sub>3</sub> , SbOCl, partly. H <sub>2</sub> WO <sub>4</sub> . Treat with boiling water.		P	
Add HCl in sufficient amount to remove SbOCl as SbCl <sub>3</sub> . Wash with water and warm with NaOH in excess.		R	
Reject.		F	
Na <sub>2</sub> SiO <sub>3</sub> , Na <sub>2</sub> WO <sub>4</sub> . Acidify with HCl.		P	
Remove H <sub>2</sub> SiO <sub>3</sub> by HF.		R	
H <sub>2</sub> WO <sub>4</sub> .		F	
Reject.		P	
Rare earth oxalates. Traces of Fe, Cr, Mn, U, Zn (traces). Boil with concentrated (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .		R	
Rare earths, Fe, Cr, Mn, U, Be (traces). Dissolve in HCl and add oxalic acid to warm acid solution.		P	
Pb, Ti, as chlorides. Add H <sub>2</sub> SO <sub>4</sub> . See Table I.		F	
Pb		Ti	
Hg, Pb, Bi, Cu, As, Sb, Sn, Se, Te, Au, Pt, Mo, as sulphides or elements with sulphur, e.g., Se and Te. For separation see Table I.		P	
Add H <sub>2</sub> S.		F	
Test for H <sub>2</sub> PO <sub>4</sub> and organic matter, and if present remove. Add NH <sub>4</sub> Cl, NH <sub>4</sub> OH, and (NH <sub>4</sub> ) <sub>2</sub> S.		P	
Fe, Ni, Co, Mn, Zn, U as sulphides: Al, Cr, Ti, Be, and rare earths, as hydroxides. Wash with water containing (NH <sub>4</sub> ) <sub>2</sub> S and treat with cold double normal HCl. Table IV.		F	
Co, Ni as sulphides. Evaporate to small volume, oxidize with 1-2 cm <sup>3</sup> of HNO <sub>3</sub> , and add NaOH in excess.		R	
Fe, Al, Cr, Mn, Zn, U, Be, Ni (traces).		F	
Al, Be, Zn, as sodium salts. Acidify with HCl, add NH <sub>4</sub> OH in excess.		P	
Al, Be, as hydroxides. Dissolve in HCl and boil with NaHCO <sub>3</sub> .		F	
P/Al(OH) <sub>3</sub>		Be	
Evaporate and ignite. ZrO <sub>2</sub> should dissolve in HF.		F	
Th, Zr, as double ammonium oxalates. Acidify with HCl.		P	
Th(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> .		F	
Y earths. Precipitate by NH <sub>4</sub> OH. Dissolve in HNO <sub>3</sub> , and identify by spectroscopic methods. See also diagram, p. 45.		P	
Ce earth double potassium sulphates, Th (traces). Boil with NaOH, wash, and treat the suspended hydroxides, in the presence of NaOH, with Cl.		R	
Ce oxyhydroxide. Distinguish by spectrum analysis. See also Tables III, IV, and V.		F	

\* Method of Böhm (Darstellung der seltenen Erden, Vol. II, p. 134) somewhat amplified and diagrammatically arranged.

## V.

## THE TUNGSTEN GROUP.

Before taking up the analysis as outlined in Table VIII, the student is instructed to review the reactions of the elements considered.

Taking separate solutions of the following salts,  $\text{Na}_2\text{SnO}_3$ ,  $\text{Na}_2\text{SiO}_3$ ,  $\text{Na}_2\text{WO}_4$ ,  $\text{K}_8\text{Ta}_6\text{O}_{19}$  and  $\text{K}_8\text{Nb}_6\text{O}_{19}$ , try the action of the following reagents, and record the results in tabular form: (1)  $\text{HNO}_3$  to acid reaction; effect of excess and result on evaporation; (2)  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  under the same conditions as in (1); (3)  $\text{NaOH}$ ,  $\text{KOH}$  or  $\text{NH}_4\text{OH}$  upon the freshly precipitated oxide or hydroxide; (4)  $\text{Zn} + \text{HCl}$  on solutions of Ta, Nb, and W; (5)  $\text{H}_2\text{S}$  on solutions containing Ta, Nb, W, Sn and Si, and subsequent acidification with  $\text{HCl}$ ; (6)  $\text{NaPO}_3$  bead with and without  $\text{FeSO}_4$ , upon small particles of the oxides or hydroxides. Try also the effect of warming the dried oxides with  $\text{HF}$  in a lead dish.

TABLE VIII.\*

Dissolve in  $\text{HF}$ , add  $\text{H}_2\text{SO}_4$ , and evaporate to the fuming-point to remove  $\text{SiF}_4$ ; cool, pour into 5  $\text{cm}^3$  of water, add  $\text{NH}_4\text{OH}$  to alkaline reaction, then colorless  $(\text{NH}_4)_2\text{S}$ , and warm in a covered dish at  $60^\circ \text{C}$ . for 15 minutes.

P   _____   F		(NH <sub>4</sub> ) <sub>2</sub> SnS <sub>3</sub> , (NH <sub>4</sub> ) <sub>2</sub> WS <sub>4</sub> .	
Ta <sub>2</sub> O <sub>5</sub> , Nb <sub>2</sub> O <sub>5</sub> , (TiO <sub>2</sub> ), (WO <sub>3</sub> ).		Acidify with H <sub>2</sub> SO <sub>4</sub> , shake and filter.	
Warm with H <sub>2</sub> O <sub>2</sub> and HCl.			
R   _____   F		R   _____   F	
Ta <sub>2</sub> O <sub>5</sub> . Dissolve in HF, add K <sub>2</sub> CO <sub>3</sub> , and boil. 2K <sub>2</sub> TaF <sub>7</sub> , Ta <sub>2</sub> O <sub>5</sub> indicates Ta.		NbCl <sub>5</sub> (TiO <sub>2</sub> )(WCl <sub>6</sub> ). Evaporate with H <sub>2</sub> SO <sub>4</sub> , dilute, pour through a Zn column, add HgCl <sub>2</sub> . Ppt. Hg <sub>2</sub> Cl <sub>2</sub> indicates Nb.	
		SnS <sub>2</sub> . (WS <sub>2</sub> ). H <sub>2</sub> WO <sub>4</sub> . Confirm by Zn+HCl. Blue color indicates W.	

\* Abridged and adapted from A. A. Noyes, Technology Quarterly, Vol. XVII, No. 3.

## VI.

## THE PLATINUM GROUP.

Before attempting any separations by the use of Table IX, the student is directed to review the reactions of the platinum group.

Take separate portions of solutions of  $\text{H}_2\text{PtCl}_6$ ,  $\text{Na}_2\text{IrCl}_6$ ,  $\text{K}_2\text{OsCl}_6$ ,  $\text{RuCl}_3$ ,  $\text{Na}_3\text{RhCl}_6$ , and  $\text{PdCl}_2$  and try the action of the following reagents upon them, recording the results in tabular form: (1)  $\text{H}_2\text{S}$ ; (2)  $(\text{NH}_4)_2\text{S}$  upon the sulphides precipitated; (3)  $\text{KOH}$  or  $\text{NaOH}$ ; (4)  $\text{KCl}$  or  $\text{NH}_4\text{Cl}$ ; (5)  $\text{KNO}_3$ ; (6)  $\text{Na}_2\text{O}_2$ ; (7)  $\text{Zn} + \text{HCl}$ .

The separation of the platinum metals is one of the most difficult analytical problems. The following scheme, offered by Leidie and Quennessen (*Bull. Soc. Chim.* xxvii, 181 (1902)), has been found to give fairly satisfactory results when the mixtures examined were not especially complex.

TABLE IX.

The finely divided metals are mixed with 5 to 6 times their weight of  $\text{Na}_2\text{O}_2$  and heated gently in a nickel crucible. Treat with water.

R		F	
The residue contains Ni, Co, and Rh, as insoluble compounds. Treat with hot $\text{HCl}$ , filter, evaporate excess of acid, add $\text{NaNO}_3$ and $\text{Na}_2\text{CO}_3$ to neutrality, and boil.		The filtrate contains soluble sodium salts of Os, Ru, Ir, and Pd. Yellow solution = Os, Ru, or Pd. Blue solution = Ir. Colorless solution = absence of all. (a) If solution is yellow, pass chlorine and heat, catching distillate in cold water.	
P	F	R	D
Ni removed.	Add excess of $\text{HCl}$ , evaporate to dryness. Add water and $\text{NH}_4\text{Cl}$ .	The residue when neutralized with $\text{HCl}$ and evaporated with $\text{NH}_4\text{OH}$ and $\text{KCl}$ should give red crystals of potassium chloropalladate if Pd is present.	
Pt as chloroplatinate	Rh in solution as reddish double chloride.	(1) If either Os or Ru is present, $\text{NH}_4\text{SH}$ gives a black sulphide. (2) If Os is present a violet osmate is produced by $\text{KNO}_3$ and heating. (3) If Ru is present a black ppt. of Ru is produced by $\text{KOH}$ and alcohol in the cold. (b) If solution is blue, neutralize with $\text{HCl}$ , evaporate in presence of $\text{NH}_4\text{OH}$ and $\text{KCl}$ . Black crystals of potassium chlor-iridate = Ir.	

## CHAPTER XIV.

## SPECTROSCOPIC TABLES.

THE importance of spectrum analysis in the chemistry of the rarer elements has suggested the insertion of some spectroscopic charts and tables.

In order to make possible the location with a fair degree of certainty of the lines in the field of visible spectra, the wave lengths of the Fraunhofer lines shown in spectrum No. 1, on the chart of Flame Spectra, are here given:

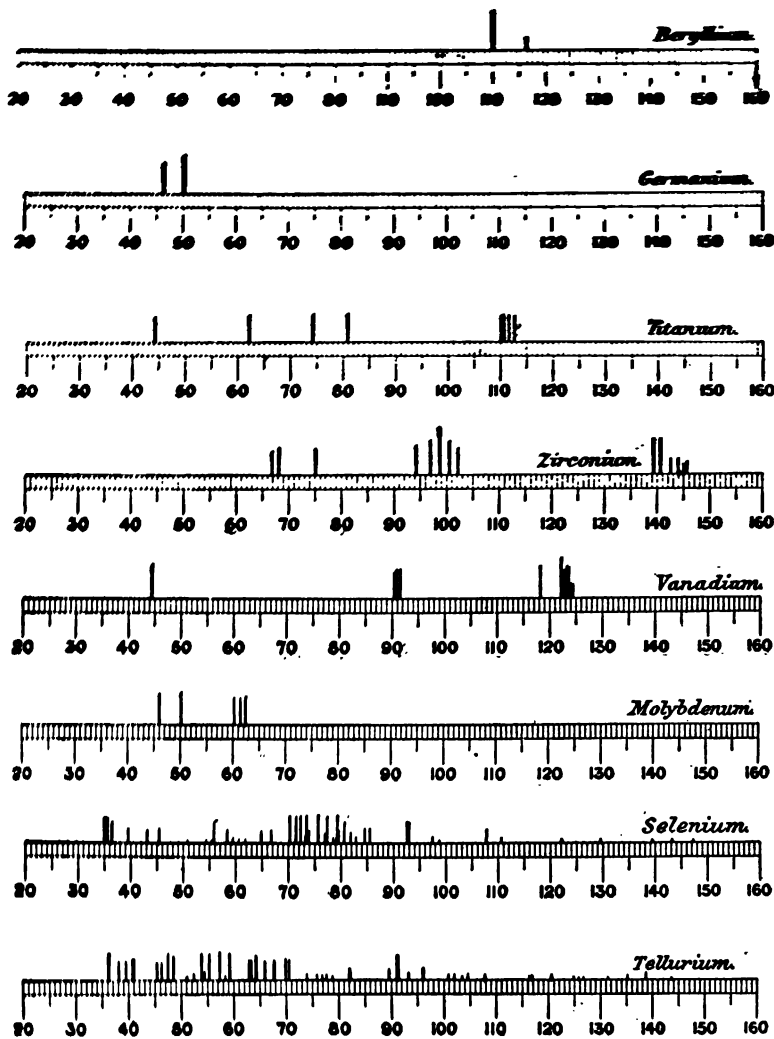
$A = 7594$ ;  $B = 6867.4$ ;  $C = 6563$ ;  $D = 5893.1$ ;  $E = 5270$ ;  
 $b = 5172$ ;  $F = 4861.4$ ;  $G = 4308$ ;  $H = 3968.6$ ;  $H_1 = 3933.8$ .

A comparison of these lines with the arbitrary scale given in the charts of Flame and Spark Spectra will serve to locate the position of the various spectra.

In the table of Chief Lines only a few of the more important are recorded. The figures in parenthesis, e. g. Li (3232-6708), show the range of the chief lines as given by Exner and Haschek. The second number, (6), gives the total number of chief lines. The other numbers, 4202.2, 4603.1, 6103.8, 6708.1, indicate the lines of greatest intensity. Few lines of an intensity below 10 on the scale used by these investigators are mentioned, and those in heavy type are of an intensity of 50 or above.

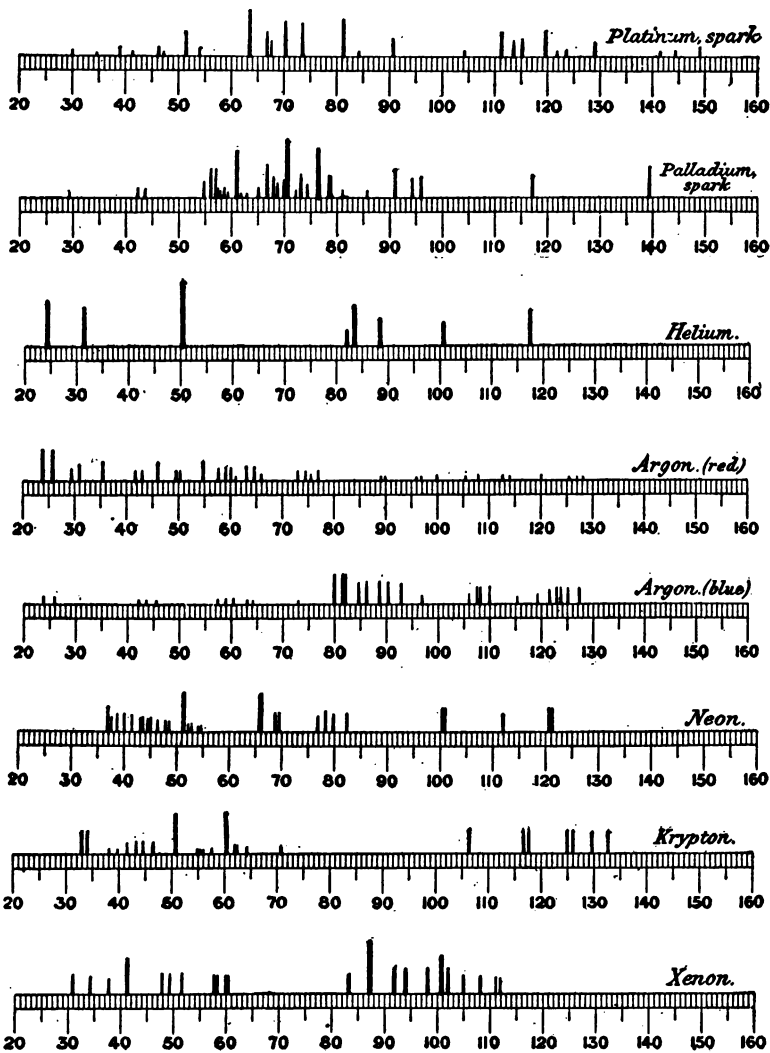
The visible spectrum lies between 7600 and 4000; the lines outside of these limits, non-existent to the eye, are observed by other methods, photography being especially valuable for this purpose whenever it is applicable. Many of the principal lines of the rare element spectra will be seen to be of a wave length below 4000, and therefore to lie in the ultra violet.

## TYPICAL SPARK SPECTRA.



Selected from An Introduction to the Study of Spectrum Analysis, Watts, Longmans, Green, & Co. (1904).

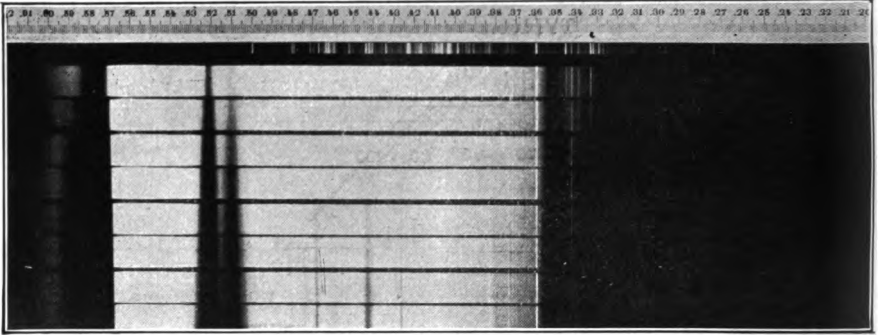
## TYPICAL SPARK SPECTRA.



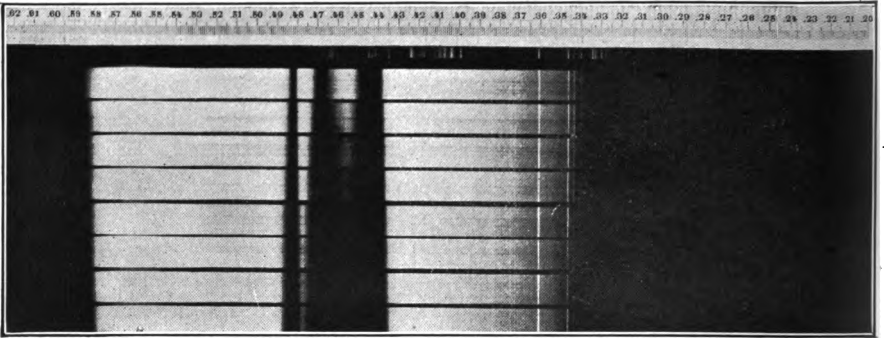


# TYPICAL ABSORPTION SPECTRA.

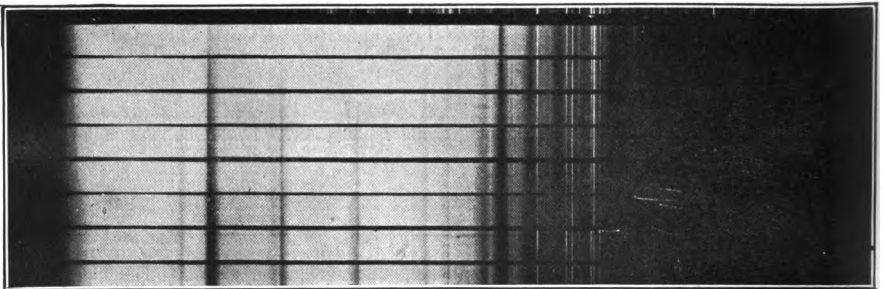
1



2



3



1. Neodymium-Ammonium Nitrate.

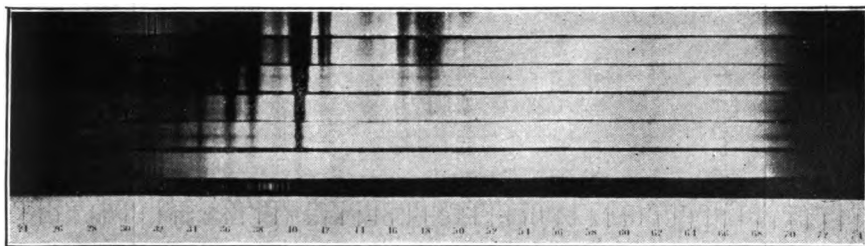
2. Praseodymium-Ammonium Nitrate.

3. Erbium Chloride.

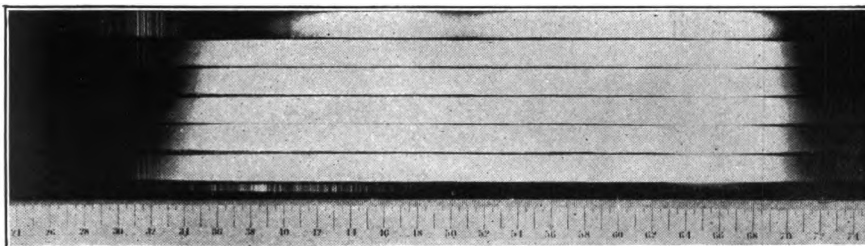
From *Atlas of Absorption Spectra*, by Uhler and Wood, Carnegie Publication, No. 71.

# TYPICAL ABSORPTION SPECTRA.

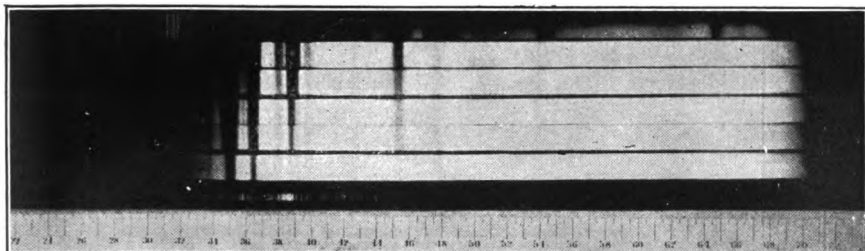
1



2



3



1. Samarium Chloride. 2. Gadolinium Chloride. 3. Dysprosium Chloride

From plates accompanying *The Absorption Spectra of Solutions of Comparatively Rare Salts*, by Jones and Strong, Carnegie Publication, No. 160.

## CHIEF LINES IN ARC AND SPARK SPECTRA.\*

Element.	Arc Spectrum.	Spark Spectrum.
Beryllium.....	(2650-3321)(5) 2650.7, 3130.5, 3131.1, 3321.2, 3321.5 (4555-6723)(3)	(2494-4572)(5) 3130.5, 3131.2 (4428, 4709, 5056.4) † (4277-4603)(3) 4277.2, 4603.9
Cæsium.....	4555.5, 4593.3, 6723.6 (2450-3700) †	
Celtium.....	2685.2, 2765.8, 3080.7, 3118.6, 3197.9 (3952-6371)(23)	
Cerium.....	4337.9, 4386.9, 4527.5, 4594.1 (3524-4957)(19)	
Dysprosium.....	4168.1, 4187, 4211.8, 4*57.5 (3312-6221)(34)	
Erbium.....	3692.8, 3896.4, 3906.4, 4151.2 (3688-6645)(14)	
Europium.....	4120.9, 4205.2, 4435.7, 4594.2, 4627.4 (3082-6114)(34)	
Gadolinium.....	4130.6, 4251.9, 4262.2, 4327.3, 4342.3 (2874-6397)(5)	
Gallium.....	2874.3, 2943.7, 4033.2, 4172.2 (2592-3266)(8)	
Germanium.....	2651.3, 2709.7, 2754.7, 3039.2 (2676-4792)(4)	
Gold.....	2676, 3122.9, 4792.8 (3039-4511)(5)	
Indium.....	3256.2, 4101.9, 4511.5 (2924-3800)(14)	
Iridium.....	3220.9, 3368.6, 3513.8, 3800.2 (3949-6394)(7)	
Lanthanum.....	3949.2, 4238.5, 6250.1, 6262.5, 6394.4	

\* According to Exner and Haschek. Die Spektren der Elemente bei Normalen Druck.

† See Lecoq de Boisbaudran, Compt. rend., CLIII, 318.

‡ See Urbain, Compt. rend., CLII, 141.

## CHIEF LINES IN ARC AND SPARK SPECTRA—Continued.

Element.	Arc Spectrum.	Spark Spectrum.
Lithium..... (Aldebaranium)	(3232-6708) (6) <b>4602.2, 4603.1, 6103.8, 6708.1</b> (3031-5556) (8)	(4602-6708) (4) 6103.8, 6708.1 (2803-4786) (15)
Lutecium.....	<b>3289.5, 3694.3, 3988.1</b> (3132-6030) (16)	3289.5, 3694.3 (2644-6030) (15)
Molybdenum.....	<b>3798.4, 3864.3, 3903.1, 5533.2, 6030.8</b> (3868-6385) (22)	3864.2, 5506.7, 5533.2, 6030.8, (4012-4463) (9)
Neodymium.....	3951.3, 4061.2, 4303.7, 4325.8, 6385.3 (3399-4254) (14)	4303.7, 4446.5, 4451.6, 4463.1 (2936-3891) (18)
Neoholmium * (Cassiopetum)	3456.1, 3748.3, 3891.1 (2615-6463) (30)	3399.1, 3456.1, 3556.9, 3891.1 (2603-4184) (16)
Neoytterbium.....	<b>3507.5, 4184.4, 5476.8, 6222.1</b> (3713-5344) (28)	<b>2772.7, 2911.5, 3077.7, 3397.1, 3554.5</b> (2927-4672) (14)
Niobium.....	<b>4059.1, 4079.8, 4101.1</b> (3752-4420) (11)	3094.3, 4059.1, 4030.3, 4672.2 (2909-4420) (5)
Osmium.....	3782.3, 4135.9, 4212, 4420.6 (3028-6784) (27)	4420.6 (2776-4213) (13)
Palladium.....	<b>3404.7, 3517, 3609.7, 3634.8</b> (2659-4521) (14)	3404.8, 3609.7, 3634.8, 4213.1 (2424-4552) (8)
Platinum.....	2659.6, 2998, 3064.8, 4498.9 (4008-4510) (14)	2659.5, 3923.1, 4498.9, 4552.6 (3877-4510) (15)
Praseodymium.....	4206.8, 4223.1, 4429.3, 4496.6 (3280-5983) (27)	4100.8, 4206.8, 4223.2, 4225.5, 4429.4 (2910-4375) (12)
Rhodium.....	3323.2, 3396.9, 3502.6, <b>3658.1, 3692.5</b> (3814-4826) (4)	3692.5, 3790.4, 3822.4, 3856.6, 4375 (3814-4826) (3)
Radium.....	3814.6, 4082.4, 4826.1 (3587-6208) (4)	3814.6, 4082.4 (3940-4294) (7)
Rubidium.....	<b>4202, 4215.7</b> (3417-4080) (7)	3940.6, 4201.9, 4244.5 (2402-4554) (18)
Ruthenium.....	<b>3436.8, 3499, 3593.1, 3596.3</b>	<b>2678.8, 2945.7, 4554.7</b>

\* According to Exner and Haschek, holmium is composed of neoholmium, terbium, and dysprosium.

## CHIEF LINES IN ARC AND SPARK SPECTRA—Concluded.

Element.	Arc Spectrum.	Spark Spectrum.
Samarium.....	(3739-4674)(29) 4152.3, 4424.5, 4434.5, 4642.4	(4319-4467)(5) 4391, 4424.5, 4467.4 (3414-3800)(5)
Selenium.....	..... (3353-6305)(21)	3544, 3637.5, 3738.7 (3353-4415)(17)
Scandium.....	3907.6, 3912, 4023.8, 4247, 4314.3 (3311-6516)(14)	3572.7, 3913.9, 3930.8, 3642.9, 4247 (2400-4682)(9)
Tantalum.....	6450.5, 6485.6, 6514.6, 6516.4	All below 10 in intensity (2383-2530)(4)
Tellurium.....	..... (3324-4752)(22)	2383.4, 2385.8 (2659-4278)(17)
Terbium.....	3509.3, 3848.9, 3874.3, 3977 (2709-5350)(9)	3509.3, 3848.9, 3874.3, 3977, 4278.7 (3519-5350)(7)
Thallium.....	3519.3, 3775.8, 5350.7 (3188-6462)(13)	3519.3, 3775.8, 5350.6 (2441-4391)(10)
Thorium.....	4863.3, 4919.9 (3131-4481)(21)	3221.4, 3300.6, 4382.1, 4391.1 (3131-4522)(16)
Thulium.....	3762, 3795.9, 3848.1, 4187.7, 4481.4 (3371-5210)(36)	3131.4, 3462.3, 3762, 3795.9, 3848.1, 4522.7 (2516-4572)(21)
Titanium.....	4999.6, 5014.3, 5193.1, 5210.5 (4008-5805)(13)	3685.3, 3900.8, 4395.2, 4572.2 (2397-5648)(18)
Tungsten.....	5053.4, 5224.8, 5514.8, 5735.3 (3932-6449)(10)	5053.4, 5224.8, 5492.5, 5514.9 (4090-5528)(16)
Uranium.....	5493.1, 5528, 6449.3 (3184-6090)(16)	All below 10 in intensity. (3093-6090)(27)
Vanadium.....	4111.9, 4379.4, 4384.9, 4408.7 (3216-6435)(29)	3545.3, 3556.9, 4379.4, 4384.9, 6090.5, (2367-5663)(27)
Yttrium.....	3710.4, 4077.5, 4128.5, 4375.1 (3392-6127)(21)	3600.9, 3710.4, 3774.5, 4375.1, 4883.9 (3392-4497)(20)
Zirconium.....	4687.9, 4739.6, 4772.5, 4815.8	3999.1, 4149.4, 4209.2, 4380.1

# INDEX.

	Dis- covery and Occur- ence.	Extrac- tion from Sources.	Element and Com- pounds.	Estima- tion and Separa- tion.	Experi- mental Work.	Spect- rum.	Techn- ical Appli- cation.
Actinium.....	32	32	32				
Aldebaranum, see Lute- cium.							
Argon.....	190	192	194	.....	.....	224, 194	
Beryllium.....	17	18	19	21, 211	22	21, 228, 224	196
Canadium.....	171						
Cæsium.....	9	9	10, 11	12, 13, 207	14	16, 228	196
Cassiopeium, see Neoytter- bium.							
Celtium.....	45, 52						
Cerium.....	36, 43, 45, 56	56	56	58, 59, 213, 214, 212	.....	228	
Columbium, see Niobium.							
Decipium.....	62	62	64	66			
Dysprosium.....	45, 51, 52	45, 52	.....	54, 213, 214	.....	227, 228	
Erbium.....	45, 51, 52	45, 52	53	53, 213, 214	.....	226, 228	196
Erythronium.....	107						
Europium.....	45, 52	45, 54	54	55, 66, 213, 214	.....	228	
Gadolinium.....	45, 54	.....	.....	66, 213, 214	.....	227, 228	196
Gallium.....	82	83	83, 84	84	.....	228	
Germanium.....	104	104	105	106	.....	224, 228	
Glucinum, see Beryllium.							
Gold.....	182	183	185	187, 219	188	228	204
Helium.....	190	193	.....	.....	.....	224, 194	
Holmium.....	45, 51, 52	52	.....	54, 213, 214	.....		
Indium.....	85	85	86, 87	88	.....	228, 88	
Ionium.....	28	28	28				
Iridium.....	170	162	173, 174	166, 222	179	228	203
Krypton.....	190	193	194	.....	.....	224, 194	
Lanthanum.....	36, 43, 61, 62	62	62, 64	65, 213, 214	67	228	196
Lithium.....	1	2	3	4, 207	5	6, 229	196
Lutecium.....	45, 52	.....	.....	.....	.....	229	
Menachite.....	96						
Molybdenum.....	125	126	126, 127	128, 219	130	224, 229	200
Monium, see Victorium.							
Neodymium.....	36, 43, 45, 61, 62	62	63, 64	65, 213, 214	67	226, 229	196

	Dis- covery and Occur- rence.	Extrac- tion from Sources.	Element and Com- pounds.	Estima- tion and Separa- tion.	Experi- mental Work.	Spec- trum.	Techn- ical Appli- cation.
Neon.....	190	193	195	.....	.....	224, 195	
Neoytterbium.....	45, 52	.....	.....	.....	.....	229	
Niobium.....	115, 117	118	119, 120	122, 221	123	229	200
Ochroite, see Cerium.....	56						
Osmium.....	170	162	172, 174	166, 222	179	229	203
Palladium.....	170	162	172, 174	166, 222	179	224, 229	203
Platinum.....	161	162	162	165, 219, 222	169	224, 229	203
Polonium.....	27, 32	32	32				
Praseodymium.....	36, 43, 45, 61, 62	62	63, 64	65, 213, 214	67	226, 229	
Radio-elements, see Chap. III.							
Radium.....	29	29	30				
Rare earths, see Chap. IV.							
Rhodium.....	170	162	173, 174	166, 222	179	229	203
Rubidium.....	6	7	7	12, 13, 207	14	16, 229	
Ruthenium.....	170	162	173, 174	166, 222	179	229	204
Samarium.....	45, 62	62	64	66, 213, 214		227, 230	196
Scandium.....	42, 62	62	64	66, 213, 214	.....	230, 42	
Selenium.....	144	145	146	149, 219	150	224, 230	202
Tantalum.....	115, 117	118	119, 120	122, 221	123	230	200
Tellurium.....	152	153	154	156, 219	158	224, 230	203
Terbium.....	45, 51, 54	52	55	55, 213, 214	.....	230	
Thallium.....	88, 89	89	90	92, 211, 219	93	95, 230	198
Thorium.....	36, 43, 70, 71	71	33, 71, 72	73, 212, 213	74	230	197
Thulium.....	45, 51, 52	52	.....	54, 213, 214	.....	230	
Titanium.....	96	98	99	100, 101, 211	102	224, 230	198
Tungsten.....	132	132	133	135, 221	135	230	201
Uranium.....	137	138	27, 139	140, 211	142	230	202
Vanadium.....	107	108	109, 110	111, 113, 211	114	224, 230	199
Victorium.....	52	.....	.....	54			
Xenon.....	190	193	194	.....	.....	224, 194	
Ytterbium, see Lutecium, Neoytterbium.....	45, 51, 52	52	53	54, 213, 214	.....	.....	197
Yttrium.....	36, 43, 45, 46, 51	46	47	48, 212, 213, 214	49	230	196
Zirconium.....	36, 43, 76	76	77	79, 211	80	224, 230	198







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